THE ROTATORY DISPERSION AND CIRCULAR DICHROISM OF SOME KETO-LACTONES,

with an additional paper on

THE PHOTOLYSIS OF 1,4 DIPHENYL-2-CHLORO-2-NITROSOBUTANE.

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KONRAD SCHWARZWALD.

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INTRODUCTION

The Theories of Optical Activity.

Since the discovery of optical activity many attempts have been made to explain the origin of the phenomenon. More recently, theories have been put forward which lead to formulae expressing the optical activity as a function of other molecular parameters. Although the results of these theories are still unsatisfactory as far as quantitative results are concerned, they are successful in explaining qualitatively the causes of optical activity. It is not yet possible, however, to establish a systematic relationship between chemical constitution and optical activity. A comparative study of the optical properties of compounds of similar chemical structure remains one of the main methods of tackling the problem and much experimental material has been accumulated in this field.

The problem of optical activity has been approached from two sides: (1) Chemists have tried to find a model which could explain - at least qualitatively - the different behaviour of a rotating substance to right- and left-handed circularly polarised light. Le Bel and van 't Hoff found a model satisfying this condition in a tetrahedron formed by the valencies of the carbon atom with four different substituents in the corners (asymmetric carbon atom). Later this model was supplemented by others, as, e.g., the

pentagonal pyramid of the asymmetric nitrogen atom, o.-o'.-disubstituted diphenyl derivatives which restricted rotation, asymmetric sulphoxydes and inorganic complex salts. In all these cases the model of the molecule exists in two configurations which are in the relation of object and mirror-image.

In order to explain the quantitative differences between the rotatory powers of various substances, Guye(1) and Crum ~~and~~ Brown(2) went further in assuming that the "dissymmetry" of the masses of the four substituents connected with the central atom was the decisive factor; they introduced the "product of dissymmetry" (a-b)(b-c)(c-d)(a-c)(a-d)(b-d), where a,b,c,d are the masses of the substituents as a function proportional to the optical activity of any compound. This hypothesis was disproved by Walden, who showed that even substances with a vanishing product of dissymmetry (e.g., substances with two substituents of equal mass but of different structure at the asymmetric carbon atom) were optically active.

(2) Physicists have deduced from Maxwell and Hertz's electromagnetic theory the conditions under which a homogeneous medium causes rotation of the plane of polarisation of light. The theory which had been applied so successfully to the problems of refraction and absorption was extended to the problem of circular double refraction by

Drude(3). He developed formulae for rotation as well as for rotatory dispersion. The latter $\alpha = \sum_n \frac{k_n}{\lambda^2 - \lambda_n^2}$ (k_n and λ_n are constants) closely resembles the classical formula for dispersion. This was not surprising since Fresnel had shown that the rotation was related to the difference of the two refractive indices for left-handed and right-handed circularly polarised light by the equation $\varphi = \frac{\pi l}{\lambda}(n_e - n_r)$ radians. Having used the dispersion theory based on the electromagnetic theory, Drude sought the explanation of optical rotatory power in a certain type of electronic motion. Oscillation of the electrons along spirals in space seemed to be a suitable model fulfilling the required physical conditions. It was, however, found later that Drude's mathematical treatment did not correspond to this model (4).

Another important step towards the understanding of optical activity was Cotton's(5) discovery of the effect now called after him: the behaviour of the rotatory dispersion curve within some absorption bands and the circular dichroism exhibited by such bands. The circular dichroism is defined by the difference ($\varepsilon_e - \varepsilon_r$) between the absorption coefficients for left-handed and right-handed circularly polarised light; ε_e and ε_r in turn are determined by Lambert's formula $I_r / I_{or} = e^{-\varepsilon_r c d}$ (c = concn.; d is the thickness of the layer of the medium, I_{or} the initial intensity of the

right-handed light, I_r its intensity after passing through the medium). The difference ($\varepsilon_l - \varepsilon_r$) was found to have a maximum at the same wave length as the maximum of the curve of total absorption ($\varepsilon = \frac{1}{2}(\varepsilon_l + \varepsilon_r)$). . The rotatory dispersion in such bands has both $^{\alpha}/$maximum and $^{\alpha}/$minimum which are usually separated by a reversal of sign ($[\alpha] = 0^{\circ}$) coinciding with the maximum of the absorption (and of the circular dichroism curves). This striking phenomenon indicated that attention had to be paid to the absorbing regions which hitherto had been neglected both experimentally and theoretically. It also suggested that an electronic model might be found which would account for the phenomena of absorption, refraction, circular dichroism and rotation of the plane of polarisation. Absorption of light had been explained by the friction in the forced motion of the electrons under the action of the light wave by Helmholtz(6). Natanson(7) therefore derived formulae for rotation and circular dichroism, introducing a "damping factor" (already used by Drude in his later theory). The results thus obtained were: $n_l - n_r = \frac{D\lambda(\lambda^2-\lambda_0^2)}{(\lambda^2-\lambda_0^2)^2+\Gamma^2\lambda^2}$ for circular double refraction and $\kappa_l - \kappa_r = \frac{D\Gamma\lambda^2}{(\lambda^2-\lambda_0^2)^2+\Gamma^2\lambda^2}$ ($J/J_0 = e^{-\frac{4\pi\kappa d}{\lambda}}$, D=constant, λ_0 the wave length of maximum absorption, Γ= damping factor) for circular dichroism. From the first formula the angle of rotation is obtained by inserting for $n_l - n_r$ in Fresnel's formula (see page 3). The observed ellipticity is defined

by the ratio $\frac{a_r - a_l}{a_r + a_l} = \tan\varphi$ where a_r, a_l are the amplitudes of left-handed and right-handed circularly polasied light after passing through the medium. According to Lambert's law, this is equivalent to $\frac{e^{-\frac{2\pi\kappa_r}{\lambda}} - e^{-\frac{2\pi\kappa_l}{\lambda}}}{e^{-\frac{2\pi\kappa_r}{\lambda}} + e^{-\frac{2\pi\kappa_l}{\lambda}}} = \frac{1 - e^{-\frac{2\pi}{\lambda}(\kappa_l - \kappa_r)}}{1 + e^{-\frac{2\pi}{\lambda}(\kappa_l - \kappa_r)}}$ and since the exponentials in this expression are always small, the first two terms of the expansion into a series will suffice as an approximation, giving $\tan\varphi \sim \frac{2\pi/\lambda(\kappa_l - \kappa_r)}{1 - 2\pi/\lambda(\kappa_l - \kappa_r)}$ $\sim \pi/\lambda(\kappa_l - \kappa_r)$ (since $2\pi/\lambda(\kappa_l - \kappa_r) << 1$). Noting that this again is a small quantity, $\tan\varphi$ may be replaced by $\sin\varphi \sim \varphi$ so that the equation for small ellipticities reads finally: $\varphi \sim \pi/\lambda(\kappa_l - \kappa_r)$; (for $d = 1$). Γ in Natanson's formula is the half-width of the circular dichroism curve and the constant D is equal to $\Gamma\chi(\kappa_l - \kappa_r)_{max} = \lambda/4\pi\,\Gamma(\varepsilon_l - \varepsilon_r)_{max}$. Natanson's formula can be tested using the experimental results for $(\varepsilon_l - \varepsilon_r)_{max}$ and Γ from the dichroism curves. The agreement between the rotatory dispersion curve thus calculated and the observed curve is satisfactory in many cases.

The next great advance was made by Born(8) and simultaneously Oseen(9), who solved the problem of interaction of a light wave with a system of electronic oscillators orientated at random in space and coupled with each other. The problem is rather involved and can only be solved by complicated calculation. It appears, however, from the theory that the plane of polarisation of the light

wave is rotated by a system of vibrators which have no plane of symmetry.

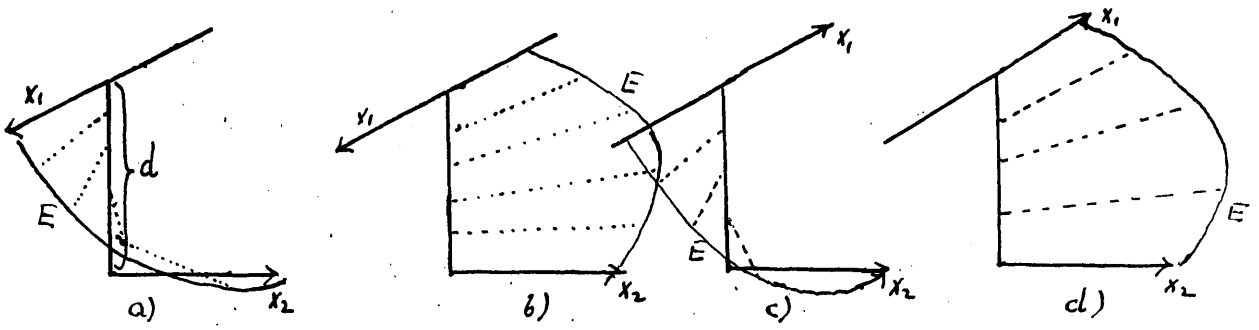
Another important result is that at least four atoms are necessary in order to cause rotation. Absorbing regions of the spectrum were not dealt with (the motion was assumed to be without friction). While being of fundamental importance theoretically, the final formulae of Born and Oseen contain too many unknown molecular parameters to be practically useful. In a few cases, however, Born's theory has been applied with success (10).

A similar treatment was suggested by Gray(11) who used a more special model (the tetrahedron arrangement). His results, which are in general agreement with the theories of Born and Oseen, did not lead to a formula which could be tested experimentally.

A different theory was put forward by de Mallemann (12): the coupling forces between the substituents were neglected but the phase difference and the inhomogeneity of the field of the light wave within the molecule were taken into account. A system of vibrating electrons then produces secondary waves whose plane of polarisation in general is not the same as the plane of polarisation of the incident light and rotation is thus caused. De Mallemann later tried to simplify his theory so as to make it applicable to practical calculations: instead of the tensors of polarisation in his original formula the mean polarisabilities

calculated from the atomic refractivities were used and direct coupling between the substituents was assumed. It seems, however, that, apart from a calculation for the compound CClBrIF (which cannot be confirmed by experiment), the theory has not been used in practice.

Kuhn's Theory. Starting from Born's theory, W. Kuhn(13) in 1929 set out to obtain expressions more amenable to practical applications for rotatory power and circular dichroism. Kuhn's basic model (see diagram) consists of a pair of coupled vibrators moving at right angles to each other and separated by a finite distance. The left-handed



helix in Fig. a) represents the electric field vector of the circularly polarised light wave; x_1 and x_2 are two electric charges vibrating along the arrows at right angles to one another. It is seen from the figure that if the distance d between the oscillators = $\lambda/4$, the vector at the one oscillator includes an angle of $\pi/2$ with the vector at the other; (in the course of one wave-length the electric vector turns through 2π in the course of $\lambda/4$ therefore through $\pi/2$). In this case the wave is in phase either with both or with

neither of the oscillators (in Fig.a) it is in phase with both of them). In Fig.b) a right-handed helix acts on the same model; here the electric vector obviously cannot be in phase with both vibrators; if it is with the first, it is of opposite phase with the second and vice versa. Similar arguments, of course, hold for the mirror image of the model where the right-handed helix is in phase with both oscillators (c and d). The work done on either of the models by the right-handed and the left-handed wave will be different since in the case a) the work done on both oscillators is positive, E the electric vector of the light wave and v the velocity of the particle being of equal sign, whereas in b) there are two terms of opposite sign since E and v are of opposite sign if the wave is out of phase by $\lambda/2$ with the velocity of the vibrator. The difference in the energy transferred by two opposite circularly polarised beams to the model accounts for the difference between absorption coefficients for the two beams (circular dichroism) and the difference between their refractive indices (rotation). In general d is not equal to, but small compared with λ, d being of the order of 10^{-8}cm. and λ of the order of 10^{-5}cm., but the arguments explaining the optical activity of the model still hold qualitatively. The model may be generalised for an arbitrary number of oscillators all coupled with one another and orientated arbitrarily. In the case of gases and isotropic liquids the random

orientation of the molecules must be taken into account. Solving the equations of motion for the single pair of coupled vibrators, Kuhn obtained for its contribution to the rotation: $\varphi_f = \frac{2\pi d}{c^2} N\nu^2 \frac{e_1 e_2}{\sqrt{m_1 m_2}} \sin\alpha\cos\alpha \frac{\nu_1^2 - \nu^2}{(\nu_1^2-\nu^2)^2 + \nu^2\nu'^2}$

where e_1 and e_2 are the electric charges of the oscillating particles, m_1 and m_2 their masses, ν_1 the frequency corresponding to the head of the band and $\nu' = \frac{c\lambda'}{\lambda^2}$, λ', being half the width of the band on the wave length scale, α the angle between the two oscillators and d their mutual distance. The formula still contains a number of parameters which can not be obtained from experiments, e.g., $\frac{e_1 e_2}{\sqrt{m_1 m_2}}$ corresponding to the f_i factors in the quantum theory of dispersion ("oscillator strength") - as well as - α are not known. Kuhn got over this difficulty by making use of his formula derived for circular dichroism: $\int_{\text{band}} (\varepsilon_e - \varepsilon_a)\, d\nu = \frac{4\pi^2 N d}{c^2} \frac{e_1 e_2}{\sqrt{m_1 m_2}} \sin\alpha\cos\alpha$; inserting into the former formula he obtained $\varphi_f = \frac{1}{2\pi} \frac{\nu^2}{\nu_1} \cdot \frac{\nu_1^2 - \nu^2}{(\nu_1^2-\nu^2)^2 + \nu^2\nu'^2} \cdot g_1 \int \varepsilon\, d\nu$ where $g_1 =$ is assumed to be constant within a simple absorption band. The integral $\int_{\text{band}} \varepsilon\, d\nu$ is approximated to by Gauss's error distribution curve $\varepsilon = \varepsilon_{max}\, e^{-\left(\frac{\nu-\nu_1}{\Theta}\right)^2}$ which allows explicit evaluation of the integral. φ_f then finally becomes: $\frac{1}{2\pi} \int_0^\infty \nu^2 \varepsilon_{max} g/\nu_1\, e^{-\left(\frac{\nu_1-\nu}{\Theta}\right)^2} \frac{\nu_1^2 - \nu^2}{(\nu_1^2-\nu^2)^2 + \nu^2\nu'^2}\, d\nu$;

After some changes of variable and replacing an integral by an approximate value, Kuhn's final formula for the contribution of an absorption band to the total rotation of the

molecule is:

$$M = \frac{100}{2\sqrt{\pi}} \frac{(\varepsilon_l - \varepsilon_r)_{max}}{\log_{10} e} \frac{\nu}{\nu_0} \left[e^{-\left(\frac{\nu_0 - \nu}{\theta}\right)^2} \int_0^{\frac{\nu_0 - \nu}{\theta}} e^{x^2} dx - \frac{\theta}{2(\nu + \nu_0)} \right]$$

M is the "molecular rotation" defined by $M = \frac{\text{mol. weight} \times [\alpha]}{100}$ where $[\alpha]$ is the specific rotation. The observed rotations are the sum of the contributions of all absorption bands of the molecule. On the other hand, subtracting the contribution of an absorption band from the observed rotation, the contributions of the other bands may be obtained. Kuhn's equation has been applied with considerable success to the problem of resolving the observed rotatory dispersion curve into the contributions due to various active absorption bands; it must, however, be borne in mind that the formula is semi-empirical as it includes the data of the observed circular dichroism and not the parameters appearing in Kuhn's basic model. Lowry and Hudson(14) found that absorption curves were more usually symmetrical when plotted against wave-lengths than frequencies. They therefore represented the extinction curve by the equation $\varepsilon = \varepsilon_{max}\, e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2}$ and made corresponding changes in the equation for the curve of circular dichroism. This leads to a modification of Kuhn's formula where λ throughout replaces ν and λ_0 ν_0*. The formula thus obtained proved in many cases to be in better agreement with the observed curves than Kuhn's original equation.

A more recent theory is that of Boys(15). Starting from a special type of molecule, the rotation is expressed

* $-\frac{\theta}{2(\nu+\nu_0)}$ becomes $+\frac{\theta}{2(\lambda+\lambda_0)}$

in terms of refractivities of the substituents and of molecular dimensions. His mathematical treatment has been criticised by Born(16) on theoretical grounds. When applied to the calculation of the rotations of some simple compounds, however, good results were obtained.

With the replacement of the classical theory of dispersion by the quantum mechanical treatment of molecular optics, it had become necessary to revise the theories of optical activity. This was first done by Rosenfeld in 1928 (17) who gave a consistent treatment of the problem of rotatory dispersion on the basis of quantum theory. His results are a "translation" of Born's(8) classical theory into the language of quantum mechanics. Amplitudes of the vibrating electrons are replaced by transition probabilities between the various states of the electron. The decisive factor is the matrix element (a/p/b)(b/m/a)* representing the change of the magnetic moment connected with the change of the electric moment in a transition of the electron from a to b under the action of the incident light. Although Rosenfeld's formulae were not suitable for practical applications, they are of fundamental importance in providing the starting point for the more modern theories. A similar treatment based on quantum mechanics was given two years later by Born and Jordan(18).

In 1935 Born(16) attempted to adapt his earlier (classical) theory so as to make it more useful to chemists.

*(a/p/b) = matrix element of the electric moment,
(b/m/a) = " " " " magnetic " .

Although the formula applied to a spiro-compound gave the right order of magnitude for the rotation, it still remained - in spite of the considerable simplifications made - too complicated and requiring the knowledge of too many factors to be of more than limited use.

It was not until 1937 that J. Kirkwood(19) derived a quantum theory of optical activity applicable to practical problems. Using Rosenfeld's results, he deduced (after some suitable simplifications) a formula which he applied to the case of secondary butyl alcohol with considerable success. Even in this simple compound, however, far reaching assumptions had to be made about the configuration of the molecule (valency angles, free rotation, etc.).

In the same year Condon, Altar and Eyring(20) showed on the basis of quantum mechanics (Rosenfeld's results) that not only the coupling of vibrating electrons but also the motion of a single electron in an asymmetric field can give rise to optical activity. They also gave a quantum mechanical treatment of circular dichroism. Rough calculations were made for some organic compounds using the dipole moments of the various substituents and their mutual orientation and distance. The basic model is a three-dimensional oscillator moving along the axes of an ellipsoid. By the action of the neighbouring substituents the motion is disturbed so that the axes of the ellipsoid are slightly twisted causing the electron to move along helicoidal paths instead of moving along the coordinate axes.

The model is the picture in classical mechanics of Rosenfeld's result asserting that the rotation for a certain wave-length is proportional to Im(a/p/b)(b/m/a): (a/p/b and b/m/a have the same meaning as above; Im denotes the imaginary part of the complex matrix product). It is clear from the model that a change in the electric moment (as the electron changes its elongation from the centre to which it is attached) involves a change of the magnetic moment (since the motion of the electron along the helix is equivalent to a current in a coil corresponding to a magnet parallel to the axis of the coil). The expression Im(a/p/b)(b/m/a), denoted by R(a,b), is a quantitative measure for the contribution to the rotation of the electronic transition from state a to state b. The total contribution of the electron is found by summing over all states b corresponding to all possible transitions of the electron. The mathematical analysis of the model is based on perturbatory theory; R(a,b) is zero for the unperturbed three-dimensional harmonic oscillator because the selection rules known to hold for the harmonic oscillator make alternatively either (a/p/b) or (b/m/a) equal to zero. The asymmetric disturbance of the field in which the electron moves makes the term which is zero in the undisturbed field different from zero in the first order approximation (in the disturbed field). If (a/p/b) is equal to zero in the undisturbed field, it is small in the first order approximation

(otherwise there is no justification for using the perturbation method) and the optically active band is weak (the absorption being proportional to $/(a/p/b)/^2$). If $(a/p/b) \neq 0$ (in that case $b/m/a = 0$) the band is strong; in both cases R(a,b) is of the same order of magnitude as it is a product of a very small term and a term comparable with unity. This fact bears out the established rule that large anisotropy factors are to be found only in weak absorption bands because $(\varepsilon_l - \varepsilon_r)$ is of the same order of magnitude both in weak and strong bands. R(a,b) is therefore in general $\ll 1$. Between Kuhn's anisotropy factor and the "rotatory strength" R there exists the relationship $R(a,b) = f \cdot g \cdot \frac{3}{2\pi} \frac{\lambda \cdot a}{a}$ The letters have the same meaning as above: a is the radius of the first Bohr-orbit of the electron. (f = "oscillator strength")

Unfortunately all these theories do not enable the chemist to establish a system of relationships between chemical constitution and optical activity; they rather suggest that such rules do not exist owing to the sensitivity of optical activity to changes in atomic distances and orientation. In fact, it seems that all the simple rules found by chemists regarding rotatory power are only of very limited validity.

Apart from Guye's theory on the dependence of the rotation on chemical constitution (see p.2) there have been mainly three assumptions as to the contributions of the different parts of a molecule to the observed rotation.

The principle of optical superposition. Van 't Hoff believed that in a molecule consisting of several active carbon atoms each of them accounts for a rotation independent of the constitution at the other active C-atoms: the total rotation is thus a sum of the rotations of the single active C-atoms. While many cases were found where this principle holds fairly accurately it is quite untrue in others.

Tschugaeff's intramolecular and extramolecular superposition. The fact that active compounds with only one asymmetric C-atom usually have a normal rotatory dispersion in the transparent regions, whereas substances with more than one active C-atom often exhibit an anomalous rotatory dispersion outside their absorption bands, led Tschugaeff(21) to believe that this phenomenon was essentially connected with the presence of more than one active centre in the molecule. If there are contributions of opposite sign anomalies . of this kind are caused. Tschugaeff assumed that such contributions come either from two or more different active C-atoms in the same or in different molecules which by intramolecular or extramolecular superposition cause the anomalous rotatory dispersion. There are, however, compounds where one single active C-atom causes an anomalous dispersion of the type described above (Kuhn(22)) the reason for this being that even in substances with one

active centre there are contributions of different sign by the different absorption bands of the molecule.

The Vicinal Rule. The fact that chromophoric groups which ~~for~~ themselves are not asymmetric show circular dichroism is explained by the assumption that the vibrations of the electrons in this group are disturbed asymmetrically by the other groups of the molecule. It is plausible that the substituents next to the absorbing group should prevail in the influence exerted on the electronic vibrations of the absorbing group by the rest of the molecule. Thus in cases where the rotation in the visible is mainly due to the contribution of an active absorption band in the blue or in the near ultra-violet, the rotation will be very sensitive to chemical changes near the absorption group but it will not be strongly affected by changes of constitution in the further distant parts of the molecule. This qualitative rule has been discussed by Kuhn(23) with many examples and proved to be very useful. It, for example, includes van 't Hoff's principle of optical superposition as a special case. Van 't Hoff's rule was found to hold for substances where the two or more active C-atoms are sufficiently separated so as not to be mutually influenced by constitutional changes at one of them. The rule does not hold for substances where the two active centres are close to each other as, e.g., in tartaric acid. Another consequence of the vicinal rule is the possibility of

predicting the change of rotation due to the exchange of two substituents from the change caused by the same exchange of substituents in a compound of similar chemical structure.

The vicinal rule seems to some extent to contradict Kuhn's model: from Kuhn's theory the distance between the two coupled vibrators can be calculated by the formula d if the absorption band is caused by electronic transitions (dipole-vibrations). These distances very often amount to 6 - 10 and sometimes 60 - 80 Angstroems where there can be no question of vicinal interaction between the two oscillators. Kuhn tried to avoid this difficulty by assuming that the scattering moments of weak absorption bands extend over large parts of the molecule and possibly even beyond the molecule (23). In this case there would be vicinal action on the particular scattering moment even by distant substituents and the vicinal rule could not hold for such cases. There is, however, no confirmation for the rather questionable assumption about the spacial extension of the vibrating dipoles of weak absorption bands except the calculations based on Kuhn's model.

It is seen from the above survey that there is yet a wide gap between strictly theoretical computations of rotations which are possible only in a few cases of very simple compounds and the qualitative rules with which the chemists are working.

Because of the inherent difficulties of the problem the accumulation of experimental material remains a main method in the research in relationships between optical activity and chemical constitution. The present paper gives an account of the rotatory power, circular dichroism and absorption spectra of some keto-lactones which are of special interest since their specific rotation and circular dichroism exceed those of any other substances measured in isotropic solution. The corresponding measurements were made for another keto-lactone where the values are by no means extraordinary and the experimental results are discussed on the basis of the theories of optical activity as far as this is possible. The work also includes the measurement of the absorption curves of some santonine derivatives.

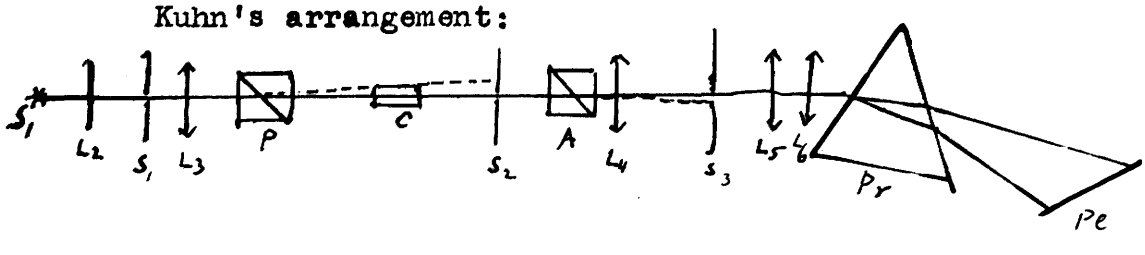
EXPERIMENTAL

A). Description of the apparatus used.

a). The Ultra-Violet Polarimeter. (24)

Method of measurement: Kuhn's method of measuring the angle of rotation in the ultra-violet is essentially the same as that of the ordinary polarimeter; the main difference is that the ultra-violet-polarimeter measures the rotatory dispersion of a medium by fixing the analyser at certain angles with respect to the "zero-setting" and finding the wave lengths for which the angle of rotation of the medium is just equal and opposite to the angle given to the analyser; (in the ordinary polarimeter the wave length is fixed by means of a monochromator and the angle of rotation is measured by finding a position for the analyser where the half-shadow fields match).

Kuhn's arrangement:



In the above sketch S_1 is the light source, s_{1-3} are screens, L_2, L_3, L_4, L_5, L_6 collecting lenses, P the polariser, A the analyser, C the cell containing the medium, Pr a

prism and Pl the plate holder. The light source consists of an iron arc (two iron rods of 0.5 cm. diameter) with a current of 3 amps. The position of the arc can be regulated in all three degrees of freedom. In order to keep the arc burning steadily the current feeding it first passes through the coil of a large electro-magnet. When long exposures are required the light source must be controlled during the time of exposure: as the pole-ends burn down iron oxide is deposited around them and the position of the light source changes: the widening of the distance between the poles causes the light to fluctuate and sometimes even to extinguish. If, however, the position of the arc is readjusted at intervals of about five minutes and if the pole-ends are cleared from oxide powder as soon as the intensity is reduced by it, this light source works satisfactorily even over periods of one hour or more. The iron arc was chosen because it has the richest and most continuous line spectrum of all the common metals. In the ultra-violet its lines only become scarce below 2400 Å.

By means of the quartz lens L_2 the light is focused on to the pin-hole of the screen S_1. Before entering the polariser it passes through another quartz lens L_3.

<u>The polariser.</u> The light was polarised by a Rochon-prism. The Rochon-prism is made of two halves of d- or l-quartz cut differently with respect to their optical axes. In

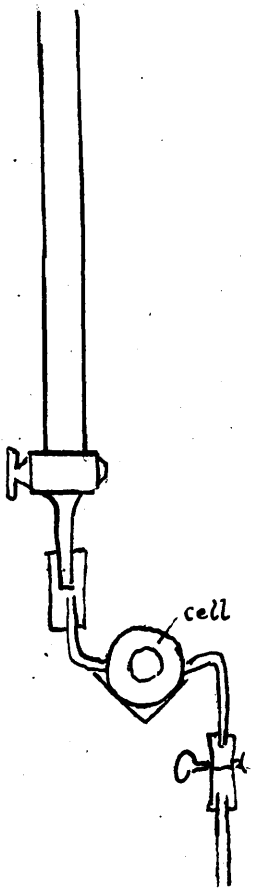
the first half the light travels along the optical axis, in the second at right angles to it. As the angle of incidence on the second half (on the right hand side of the sketch) is oblique, the extraordinary ray is deviated, whereas the ordinary (being at right angles to the optical axis) is not. A half shadow arrangement is provided by cementing together two Rochon-prisms with their optical axes inclined to each other by 5^{o}. This is done by cutting a wedge of 5^{o} out of a Rochon-prism and cementing the two parts together. Of the two light beams polarised at right angles with respect to each other, only the ordinary enters the Analyser (after passing through the cell C which contains the rotating medium). The analyser is a Rochon-prism which is so situated that the half with its optical axis at right angles to the direction of the light beam comes first. The extraordinary ray is then again deviated by the second half of the prism and does not enter the slit S_3 of the spectroscope. L_4 consists of two convex lenses, one of quartz, the other of fluor-spar, focusing the light on to the slit of the spectroscope. L_5 and L_6 are collecting lenses inside the spectrograph (made of quartz and pr is the dispersing quartz prism. Pl is the holder for the photographic plate.

Adjustment. First the image of the light source is focused on the pin-hole of the screen S. The light should pass through the centre of the collecting lens L_2. This is obtained by altering the height and mutual distance of light-source, pin-hole and lens. The distance between polariser and analyser is so chosen that the ordinary and the extraordinary ray are sufficiently separated so as to prevent the latter from entering the analyser prism. The distances between the analyser, the double lens L_4 and between the double lens and the slit of the spectroscope may also be altered in order to focus the image on the slit.

To find the zero-position ("crossed" position of the two Rochon-prisms) the polariser is held in a fixed position and by rotating the analyser the position of minimum intensity of the emerging light is found, visually at first. This may be done most conveniently by placing a slip of white paper on the slit of the spectroscope and rotating the analyser until the upper and the lower semicircles of the half shadow-field match (at minimum intensity). Having thus found the zero within 2-3°, the exact position is found photographically. To economise with the photographic plates, each was cut into 4-5 strips, each strip being $\frac{3}{4}$-1" in width and allowing 4-5 photographs to be taken on each strip. Finding the zero to 1° (taking exposures with analyser settings differing by 1°) then to 0.5°, 0.1° and 0.05°, the limit of accuracy of the instrument is reached.

This limit is determined by the large half-shadow angle of 5°. The time of exposure was 40 seconds for Ilford's Special Rapid Fast plates (700 H & D) and an aperture of the spectroscope slit of 0.3 mm. On the plate horizontal strips are seen, divided by a horizontal line. The strips represent the spectrum of the iron arc seen through the upper and the lower half-shadow field. At zero-position the spectra above and below the dividing line are of equal intensity throughout; for the actual measurements of the rotatory dispersion, the cell containing the solution of the active substance is inserted between polariser and analyser; the latter is then moved out of the zero position by a certain angle and a photograph is taken. On the plate the two half-shadow fields then no longer match; if either of them is darker than the other throughout its whole length, the angle given to the analyser is greater than the rotation of the solution for any wave-length in the region. If, however, there is a change over from darker in the top half to darker in the bottom half, there must be a spot on the strip where the two halves match. The wave-length for this spot is read from a calibrated scale (photographed on the plate): the rotation of the solution for this wave-length is equal to the angle given to the analyser. Giving the analyser a suitable set of positions, the rotatory dispersion can be measured in the whole region of the instrument. In practice the region for which measurements can

be taken is limited by the absorptivity of the substance on the one hand and by the sensitivity of the instrument on the other. The solution of the optically active substance was contained in a brass cell of 1 cm. length with ends of fused silica. As in some cases of strongly absorbing substances, exposures up to 1 hour and more had to be given, it was necessary to prevent the substance in the cell from being decomposed by the light of the iron arc. This was done by using a cell with an inlet and an outlet tube through which the solution could flow slowly or which could be refilled from time to time without interrupting the exposure. The solution was kept in a burette which was connected to the inlet tube of the cell by a piece of rubber tubing. Similarly the outlet tube was connected with a glass tube leading to a vessel where the exposed solutions were collected. The rate of flow could be regulated with a screw-clip.

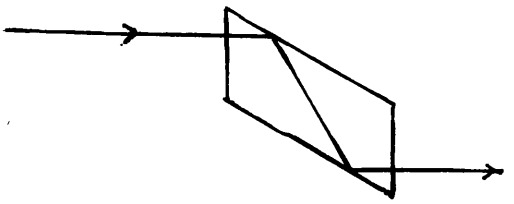


Circular Dichroism.

Method of Measuring Circular Dichroism in the Ultra-Violet.

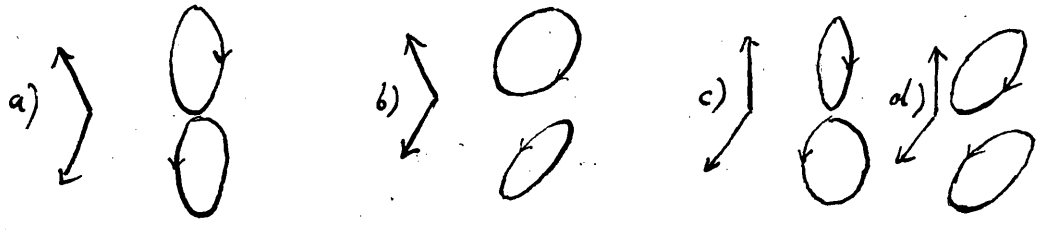
Kuhn and Braun's (13A) method of measuring circular dichroism is based on the compensation of an ellipticity

produced artificially with the equal and opposite ellipticity exhibited by the dichroic medium for a certain wavelength. The elliptically polarised light is produced by the double reflection of a Fresnel rhomb. It is generally



known that plane polarised light, when totally reflected, becomes elliptically polarised owing to a difference in phase arising between the components of the light wave vibrating parallel and at right angles to the plane of incidence. The extent of ellipticity depends for each material on the angle of incidence and on the angle between the plane of polarisation and the plane of incidence. Plane polarisation and circular polarisation of the reflected light are special cases. (The definition of ellipticity has been given on p.4). In the Fresnel-rhomb the angles are such that the light which vibrates in a plane in which also the axis of the rhomb lies, remains plane polarised after leaving the rhomb and can be extinguished by the analyser. If the circularly dichroic medium is inserted in the path of the light, the beam falling on the analyser will be elliptically polarised and it will not be possible to extinguish it for any position of the analyser since there will always be a component of the

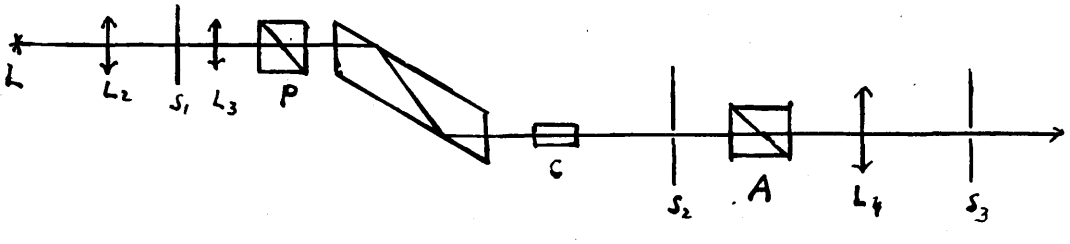
elliptical wave which can pass through the analyser. By giving the polariser a certain angle (keeping the position of the Fresnel-rhomb fixed) an ellipticity equal and opposite to that caused by the medium can be obtained. In this case the ellipticity of the substance will cancel the ellipticity of the impinging light and the beam leaving the cell is plane polarised although in a different plane (since the active medium also rotates the axes of the ellipse representing the wave.). As the light entering the analyser is plane polarised, it can be extinguished by rotating the analyser through a certain angle. Since, however, the polariser is fitted with a half-shadow arrangement, the matter is slightly different. The light emerging from the polariser is not plane-polarised but consists of two plane polarised beams including equal but opposite angles with the plane of the rhomb (a). The light after leaving



the rhomb therefore consists of two beams with equal but opposite ellipticity (see fig. b). After passing through the medium the axes of both ellipses will have been rotated through the same angle; at the same time the ellipticity of one beam will be increased, that of the other diminished by the same amount. (c). The same effect occurs in the light

leaving the Fresnel-rhomb if the polariser is rotated through a certain angle, since in this case also, two ellipses with axes of different length but of equal direction represent the two beams. Consequently, it is possible to find a position for the polariser so that the ellipticities of the two beams leaving the cell with the medium are equal but opposite (fig. d). The components of these two waves transmitted by the analyser are equal to one another and the two half-shadow fields therefore are of the same intensity.

The Apparatus and its adjustment. The arrangement is exactly the same as in the ultra-violet polarimeter except for the Fresnel-rhomb which is inserted between polariser and cell. In order to keep the light beam which leaves



the rhomb on the level of the analyser and of the slit of the spectroscope, it is necessary to raise the light-source, lens L_2, screen S_1, and the polariser. (The Fresnel-rhomb was of fused silica which is preferable to the brass trough with windows of fused silica used by Kuhn and Braun).

To find the zero position (where the light leaving the rhomb is plane polarised) the polariser is rotated until

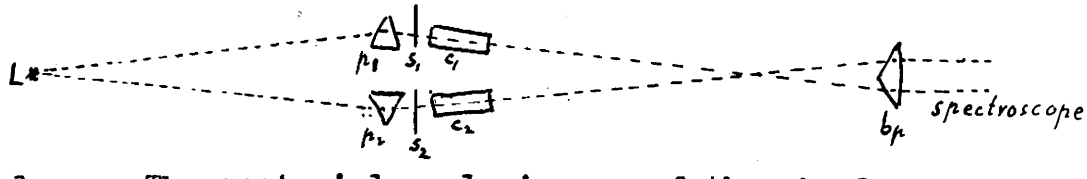
the two half-shadow fields match: this is done visually as described for the polarimeter. The position having been found, the analyser is turned until both half-shadow fields have a minimum intensity. By this the accuracy of the instrument is increased (for small intensities relative differences in illumination are observed more easily); a readjustment of the position of the polariser is necessary. The accurate zero-position is obtained photographically as in the case of the polarimeter. To take measurements, the cell with the solution is inserted between the Fresnel-rhomb and the analyser and photographs are taken for various settings of the polariser. On the plate the wave-lengths are found where the two half-shadow fields are of equal intensity. In order to make full use of the accuracy of the instrument for each setting of the polariser the analyser should be rotated through an equal angle. This ensures that the minor axis of the ellipse representing the light-wave will be transmitted and that the intensity of the light entering the spectroscope consequently has a minimum. For small angles, however, this can be neglected. The times of exposure are the same as for the measurements of rotation. The circular dichroism is calculated from angle of the polariser by the formula

$\varepsilon_e - \varepsilon_r = \frac{4 \times \cdot 4343 \times \alpha}{c \times \ell} \times \frac{\pi}{180}$ (see p.4) where α is the angle in degrees. (c = mol./litre, ℓ = thickness of layer).

Absorption Spectra.

a). Method. The Hilger Rotating Sector Spectrophotometer measures the absorption of a medium by comparing the intensity of two equal light beams, one of which passes through the medium whereas the other's intensity is diminished "artificially" by a known amount. If these two beams after that are of equal intensity the absorption of the medium must be equal to the "artificial" diminution of intensity incurred by the other beam. We than know the ratio I/I_o (where I_o is the original intensity, I the intensity after passing through the medium) which -according to Lambert's law - is equal to $e^{-\varepsilon c d}$ (where c is the molar concentration, d the thickness of the layer of the medium and ε the molecular extinction coefficient which thus may be calculated).

b). Apparatus. The optical arrangement is shown in the sketch below. The light from the light-source L passes through the two prisms p_1 and p_2 and through the rotating wheels s_1 and s_2. The latter are made of solid metal with sector-shaped apertures of equal sectorial



angle. The sectorial angle in one of the wheels can be altered. The ratio I/I_o of the time-average of the intensities of the beams after passing through the rotating

wheels is equal to the ratio of the sectorial angles of the apertures in the wheels. The two beams then pass through two cells(c_1, c_2); the beam coming through the wheel with variable sectorial angle passes through a cell containing a completely transparent liquid, the beam coming through the wheel with fixed sectorial angle passes through the cell containing the absorbing medium. The cell containing the non-absorbing liquid (usually the pure solvent of the absorbing substance whose solution is in the other cell) is inserted in order to exclude errors due to partial reflection at the quartz ends of the cell. The beams leaving the cells are not parallel but they cross in front of the biprism bp. which renders them parallel. The biprism is placed in front of the slit of the spectroscope. As light-source a nickel spark run at 10,000 volts was used. The wheel with the variable aperture is provided with a logarithmic scale so that log I/I_o can be read from the scale for each setting. The cells are of brass (in most cases 1 cm. long, fitted with quartz ends). The spectroscope is the same as used for measuring rotatory dispersions in the ultra-violet. Measurements are taken by finding on the plate wave-lengths for which the intensity of the two beams are equal. For this wave-length the absorption coefficient can be calculated from the scale reading on the variable sector and the concentration of the solution. In order to measure the absorption coefficients

for the whole range of the instrument it is usually necessary to use solutions of different concentrations.

Adjustment. In zero-position the two beams should be of equal intensity for all wave-lengths. This position is often rather difficult to find since the intensity shown on the plate is very sensitive to the levelling of the rotating sector wheels, the position of the light source and to dust suspended in the liquid or deposited on the ends of the cells. The systematic overcoming of all these difficulties has been described by Gordon(24). Having found the zero-position, readings are taken as described above. It is advisable to control the correctness of the adjustment by taking a photograph with solvent in both cells on every plate.

Preparation of the Substances.

The Santonine ($C_{15}H_{18}O_3$) used was supplied by the British Drug Houses. The melting point was checked and found to be equal to that given in the literature (170°).

Santonic Acid ($C_{15}H_{20}O_4$) was prepared according to the method of Abkin and Medvedev(25) by prolonged boiling of santonine with a saturated solution of $Ba(OH)_2$. The refluxing was stopped as soon as all the barium-santoninate had gone into solution, which usually took less than 12 hours (the duration of refluxing indicated by the authors). Moreover, the dissolving of the crude acid in sodium carbonate solution and extraction of the solution with ether was omitted since santonic acid obtained by repeated

crystallisation of the crude acid from aqueous alcohol was found to be purer than samples obtained after extraction with ether.

Santonide and Parasantonide were prepared by Canizzarro and Valente's original method (26), by refluxing santonic acid for several hours with glacial acetic acid and - after distilling off the latter - heating the residue to 180° in the case of santonide and 260-300° in the case of parasantonide. Parasantonide at this temperature distils over if the pressure is reduced (it even distils partly at barometric pressure); it did not appear to be necessary to continue the heating for four hours as recommended by the authors since this did not improve the yield. The whole procedure of heating and distilling can be finished within 1½ hours. The viscous distillate is treated with a dilute solution of sodium carbonate and ether. After removing the excess of ether the substance was recrystallised from ether plus petroleum ether and later from petroleum ether since the losses of material are too great if the substance is recrystallised from ether (as was done by the authors). To obtain a sample melting at 110.5° at least 10 recrystallisations are required which diminish the yield considerably.

Parasantonide-imide was obtained by the action of gaseous ammonia on an alcoholic solution of parasantonide

as described by Francesconi (27). M.p. 216-217°.

Parasantonic acid is formed by the action of concentrated hydrochloric acid on parasantonide and recrystallisation from water (28). M.p. 170°.

Hydrosantonic acid is prepared by reducing santonic acid with sodium amalgam (29), m.p. below 170° (dec.), and

Hydrosantonide by the action of glacial acetic acid on hydrosantonic acid in a sealed tube at 140-150°. (30). M.p. 155-156°.

l-Desmotroposantonine (31) is formed when santonine is stirred with 50% sulphuric acid at 50-60°. M.p. 194°.

EXPERIMENTAL RESULTS

A). Absorption Spectra.

As a preliminary to the study of the Cotton effect the absorption curves were investigated in order to find out whether the substance has an absorption band with which the Cotton-effect may be connected. The presence of absorption bands was tested qualitatively by means of the Baly tube. Where bands were present, the extinction curves were measured quantitatively with the rotating sector spectrophotometer.

Parasantonide (Table I, Fig.I).

The absorption spectrum of parasantonide in alcoholic solution has two definite and well-separated absorption bands; one has its maximum (ε = 1170) at λ = 2980 Å; the other has a maximum of ε = 5000 at λ = 2320 Å. The first band shows a slight bulge in the region between λ = 3130 Å and λ = 3190 Å indicating the presence of a subsidiary band. The correspondence between these absorption bands and the chromophoric groups in the molecule will be discussed more fully later. It may be mentioned here that the wave-length of the maximum of the first band is the same as that of ketonic bands in heavier organic molecules: the intensity, however, exceeds the ordinary ketonic absorption considerably. The second band may be due to one of the ring-systems in the molecule.

TABLE I.

Absorption Spectrum of Parasantonide in Alcohol.

Solution a). 0.03232 g. in 100 cm^3. alcohol, l = 1 cm.

$$= \frac{\text{sector reading}}{c.l}$$

λ(Å)	Sector read. log I/I_o	ε	λ(Å)	Sector read. log I/I_o	ε
3241	0.3	228	2832	1.0	761
3217	0.4	305	2797	0.9	685
3202	0.5	381	2783	0.8	609
3192	0.6	457	2763	0.7	533
3187	0.7	533	2754	0.6	457
3177	0.8	609	2673	0.5	381
3164	0.9	685	2626	0.5	381
3132	1.0	761	2621	0.6	457
3117	1.1	837	2609	0.7	533
3092	1.2	913	2600	0.8	609
3083	1.3	990	2588	0.9	685
3060	1.4	1067	2578	1.0	761
3035	1.5	1141	2568	1.1	837
2945	1.5	1141	2566	1.2	913
2920	1.4	1067	2558	1.3	990
2902	1.3	990	2556	1.4	1067
2882	1.2	913	2546	1.5	1141
2850	1.1	837			

Solution b). 0.0227 g. in 100 cm^3. alcohol.

λ(Å)	Sector reading	ε
2543	1.1	1192
2540	1.2	1300
2537	1.3	1410
2530	1.4	1518
2522	1.5	1627

TABLE I (Contd.)

Solution c). 0.0113 g. in 100 cm^3. alcohol.

λ (Å)	Sector reading	ε
2505	0.8	1732
2500	0.9	1950
2480	1.0	2164
2476	1.1	2380
2469	1.2	2600

Solution d). 0.0057 g. in 100 cm^3. alcohol.

λ (Å)	Sector reading	ε
2467	0.7	3028
2436	0.8	3480
2406	0.9	3896
2379	1.0	4350
2368	1.1	4760
2258	1.1	4760
2251	1.0	4350
2205	0.9	3896
2194	0.8	3480

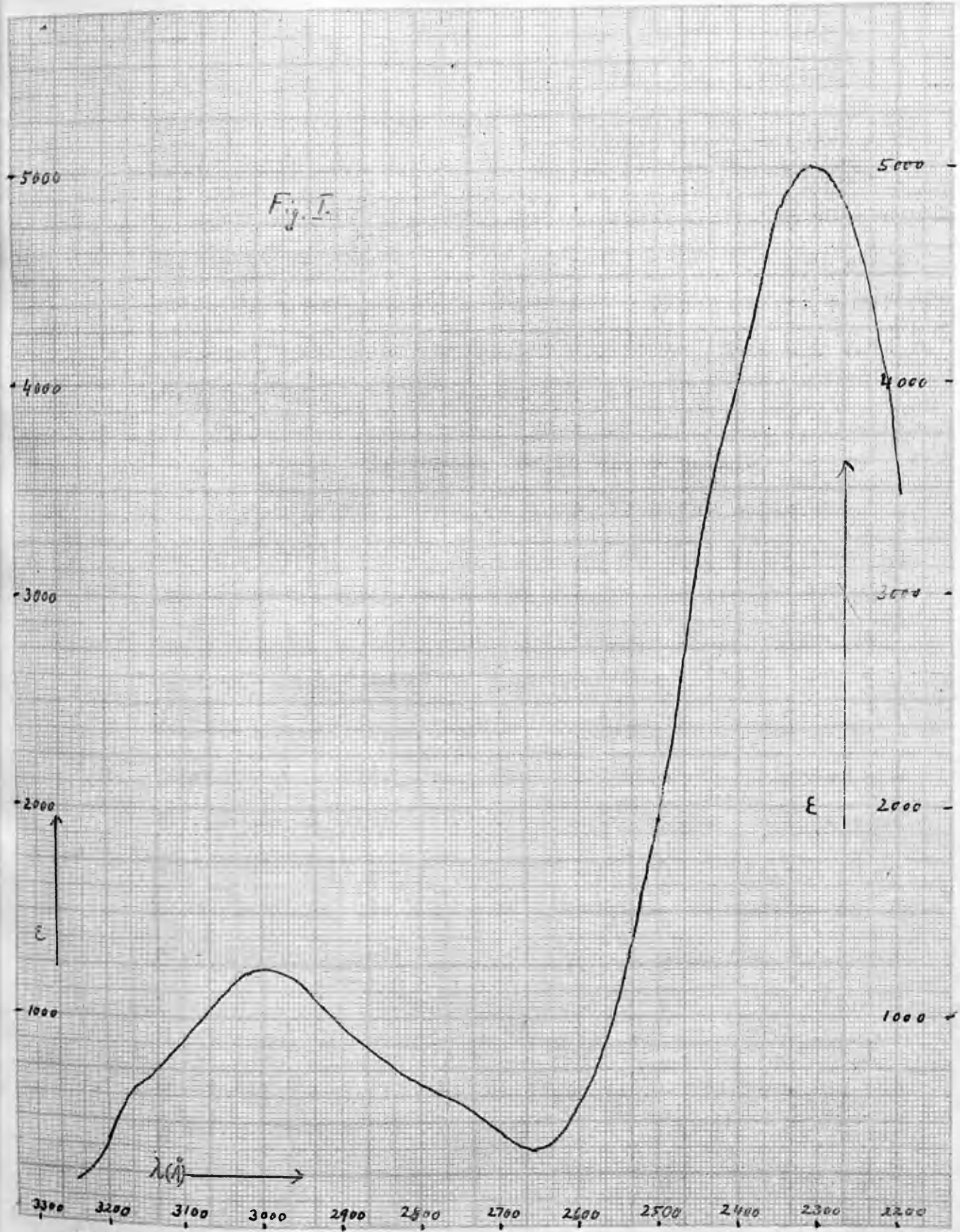


Fig. I. Absorption Spectrum of Parasantonide in Alcohol.

The fact that the hydroxy acid corresponding to the lactone parasantonide does not show this second band (see below), suggests that it is caused by the lactone-ring. In order to make full use of the accuracy of the instrument, different solutions have to be used. As the readings for concentrations varying between c = 0.3232 g/L and 0.057 g/L lie on a continuous curve, the absorption does not seem to vary appreciably with the concentration.

Santonide (Table II, Fig. II).

It is seen from the graph that the extinction curve of santonide is very similar to that of parasantonide: the two bands have their maxima at almost the same wave-lengths as the bands of parasantonide. The first band has a maximum of ε just over 1000 at λ = 2980 Å; for the second ε_{max} = 5600 at λ = 2280 Å. The bulge between λ = 3120 Å and λ = 3190 Å can be observed although not as clearly as in parasantonide. Since santonide has very probably almost the same constitution as parasantonide, the same assumptions may be made as to the correspondence between the chemical groups and the bands.

Parasantonide-imide (Table III, Fig. III).

The absorption spectrum of parasantonide-imide shows two bands like the spectra of the two previous compounds; both bands are at longer wave-lengths and more intense. The band nearer to the visible has its maximum

TABLE II.

Absorption Spectrum of Santonide in Alcohol.

Solution a). 0.0340/100 $cm.^3$ 1 = 1 cm.

λ (Å)	Sector read.	ε	λ (Å)	Sector read.	ε
3270	0.1	72.4	2843	0.9	651
3243	0.2	145	2823	0.8	579
3233	0.3	217	2793	0.7	507
3202	0.4	289	2766	0.6	434
3187	0.5	362	2730	0.5	362
3173	0.6	434	2707	0.4	289
3163	0.7	507	2643	0.4	289
3130	0.8	579	2633	0.5	362
3102	0.9	651	2617	0.6	434
3083	1.0	724	2606	0.7	507
3078	1.1	796	2601	0.8	579
3060	1.2	868	2598	0.9	651
3037	1.3	941	2589	1.0	724
2941	1.3	941	2582	1.1	796
2917	1.2	868	2577	1.2	868
2879	1.1	796	2562	1.3	941
2858	1.0	724			

Solution b). 0.0069 g. in 100 cm^3.

2588	0.2	713	2445	1.0	3565
2528	0.3	1070	2435	1.1	3922
2508	0.4	1426	2419	1.2	4278
2497	0.5	1783	2404	1.3	4635
2494	0.6	2034	2375	1.4	4991
2477	0.7	2542	2337	1.5	5348
2467	0.8	2852	2220	1.5	5348
2455	0.9	3205	2172	1.4	4991

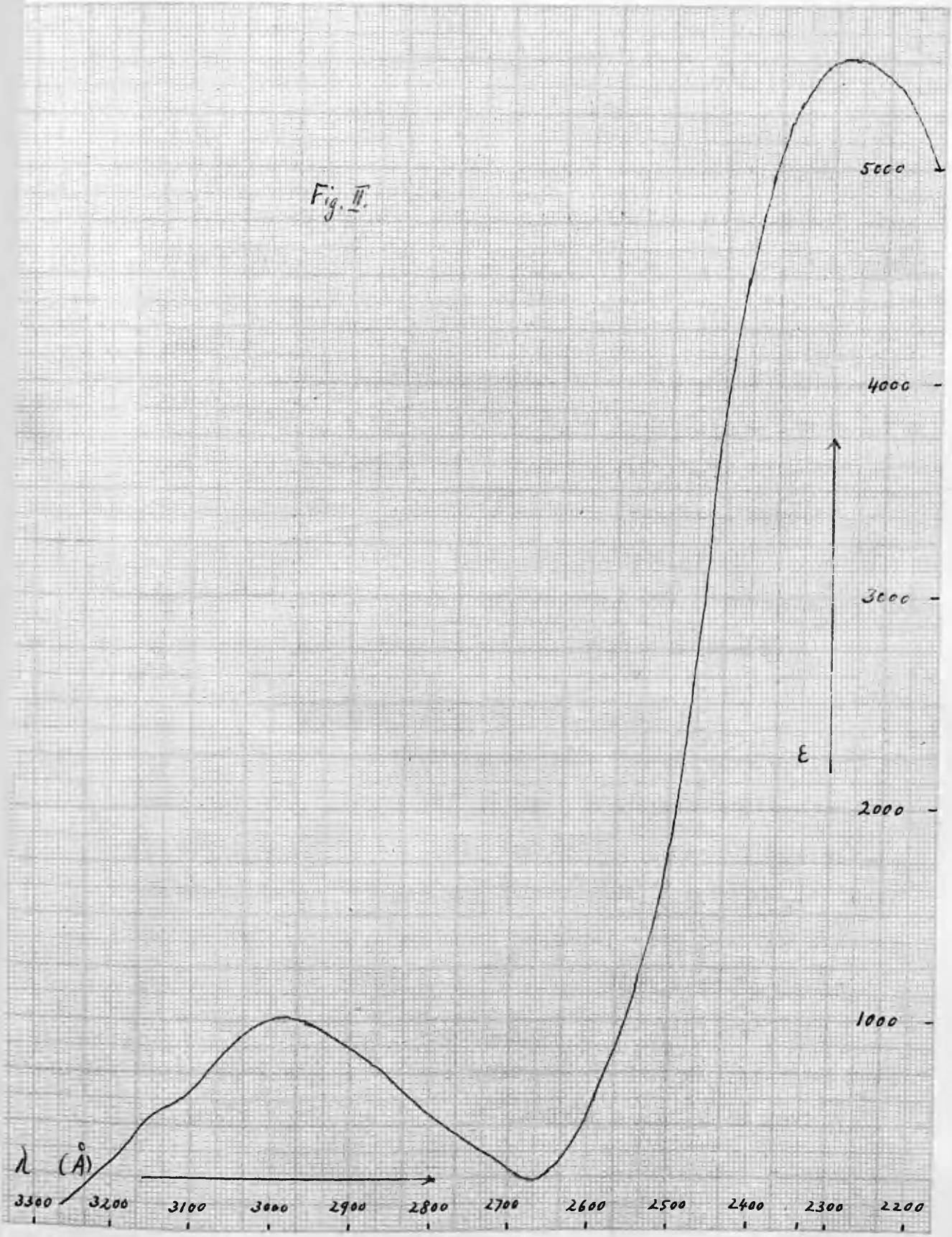


Fig. II. Absorption Spectrum of Santonide in Alcohol.

at λ = 3065 Å (ε = 2900), the other at λ = 2520 Å (ε = 7670). From the similar electronic structure of the ketonic and the C = NH group it may be inferred that the band at longer wave-lengths is the C = NH band: the other band should be the lactonic band as in parasantonide and santonide.

Parasantonic Acid (Table IV, Fig.IV)

There is only one absorption band with its maximum ε = 57 at λ = 2940 Å. Towards the short wave-length end of the spectrum the absorption increases reaching ε = 221 at λ = 2224 Å (not seen on the graph). The first band is at shorter wave-lengths than the corresponding band of parasantonide, but only 1/20 of its intensity.

Santonic Acid (Table V, Fig.V)

It is seen from Fig.V that the absorption band of santonic acid is similar to that of parasantonic acid. A subsidiary band is indicated by the shape of the extinction curve between λ = 3020 Å and λ = 3190 Å. This may be due to the fact that santonic acid has two ketonic groups, one of which is conjugated with a double bond C = C whereas the other one lies in a saturated ring. Hence they should not be expected to lie at the same wave-lengths. The maximum of the band is at λ = 2920 Å,

TABLE III.

Absorption Spectrum of Parasantonide-imide in Alcohol.

Solution a). 0.0093 g. in 100 cm^3. alcohol. 1 = 1 cm.

λ(Å)	Sector read.	ε	λ(Å)	Sector read.	ε
3321	0.1	264	2910	0.7	1843
3289	0.2	527	2883	0.6	1580
3270	0.3	791	2842	0.5	1319
3268	0.4	1055	2802	0.4	1055
3266	0.5	1319	2773	0.4	1055
3235	0.6	1580	2734	0.5	1319
3226	0.7	1843	2732	0.6	1580
3183	0.8	2105	2726	0.7	1843
3169	0.9	2370	2721	0.8	2105
3134	1.0	2635	2706	0.9	2370
3076	1.1	2900	2702	1.0	2635
3054	1.1	2900	2700	1.1	2900
2988	1.0	2635	2697	1.2	3160
2958	0.9	2370	2687	1.3	3430
2936	0.8	2105	2683	1.4	3690

Solution b). 0.0047 g. in 100 cm^3. alcohol.

2689	0.8	4220	2560	1.4	7390
2676	0.9	4750	2483	1.4	7390
2651	1.0	5270	2442	1.3	6850
2640	1.1	5800	2359	1.1	5800

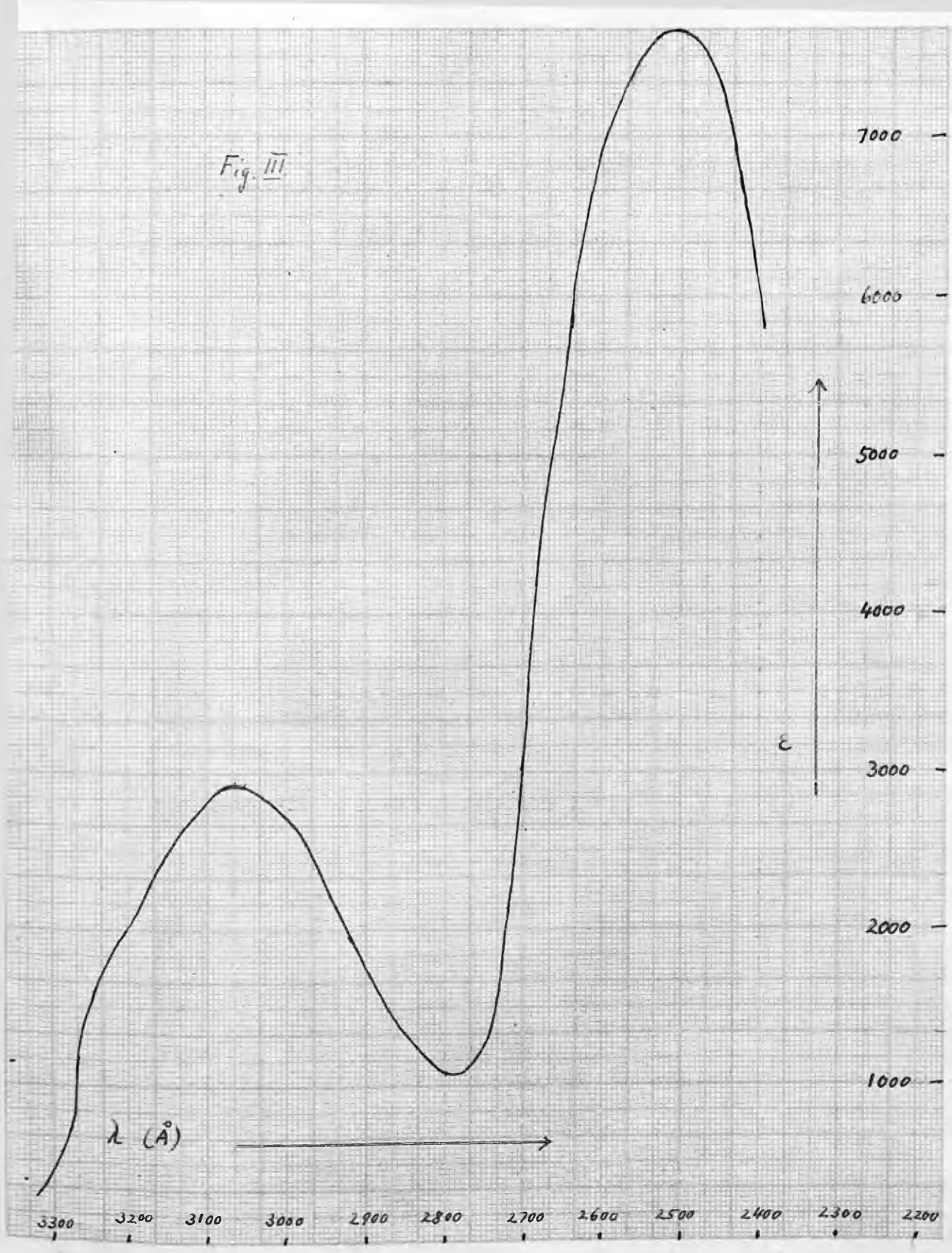


Fig. III. Absorption Spectrum of Parasantonide-imide in Alcohol

TABLE IV.

Absorption Spectrum of Parasantonic Acid in Alcohol.

Solution a). 1.074 g. in 100 cm^3. 1 = 1 cm.

λ(Å)	Sector read.		λ(Å)	Sector read.	
3268	0.2	4.9	2750	1.3	32.0
3238	0.3	7.4	2732	1.2	29.6
3220	0.4	9.8	2712	1.1	27.0
3199	0.5	12.3	2697	1.0	24.6
3183	0.6	14.8	2675	0.9	22.2
3173	0.7	17.2	2657	0.8	19.7
3163	0.8	19.7	2627	0.7	17.2
3152	0.9	22.2	2577	0.7	17.2
3135	1.0	24.6	2530	0.8	19.7
3134	1.1	27.0	2509	0.9	22.2
3117	1.2	29.6	2487	1.0	24.6
3107	1.3	32.0	2483	1.1	27.0
3087	1.4	34.4	2473	1.2	29.6
3060	1.5	36.9	2466	1.3	32.0
2783	1.5	36.9	2452	1.4	34.4
2766	1.4	34.4	2437	1.5	36.9

Solution b). 0.537 g. in 100 cm^3.

3083	0.8	39.4	2448	0.8	39.4
3038	0.9	44.2	2426	0.9	44.2
3024	1.0	49.2	2406	1.0	49.3
3002	1.1	54.1	2393	1.1	54.1
2865	1.1	54.1	2374	1.2	59.0
2842	1.0	49.3	2363	1.3	64.0
2796	0.9	44.2	2348	1.4	68.9
2760	0.8	39.4			

TABLE V.

Absorption Spectrum of Santonic Acid in Alcohol.

0·600 gm. in 100cm³

λ (Å)	Sector reading	ε
3303	0.1	4.4
3222	0.2	8.7
3192	0.3	13.1
3134	0.6	26.2
3097	0.7	30.5
3022	0.8	34.8
2968	0.9	39.2
2862	0.9	39.2
2804	0.8	34.2
2759	0.7	30.5
2701	0.6	26.2
2590	0.3	13.1
2438	0.3	13.1
2389	0.6	26.2
2378	0.7	30.5
2355	0.8	34.2
2348	0.9	39.5

Fig. IV

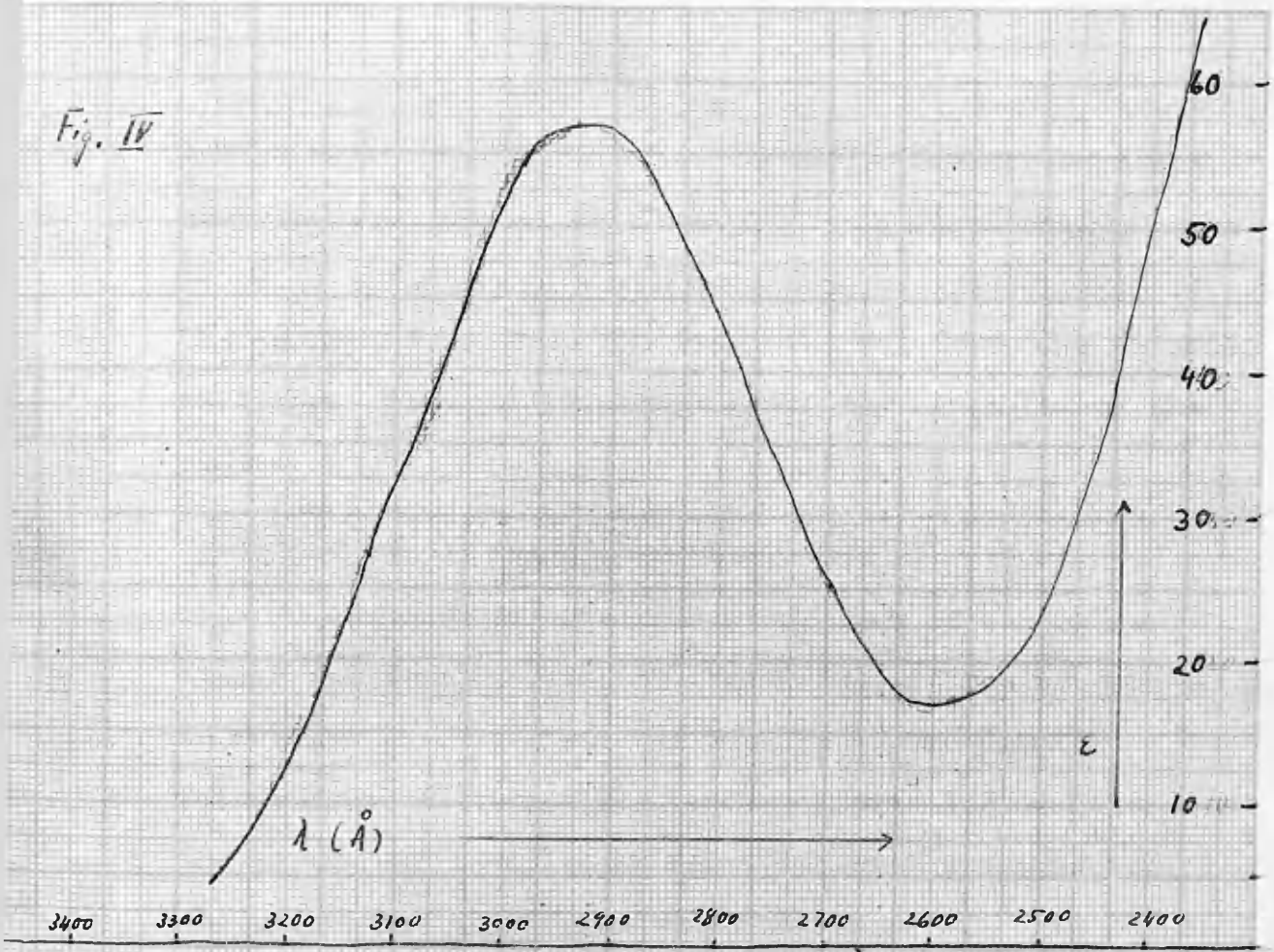


Fig. V

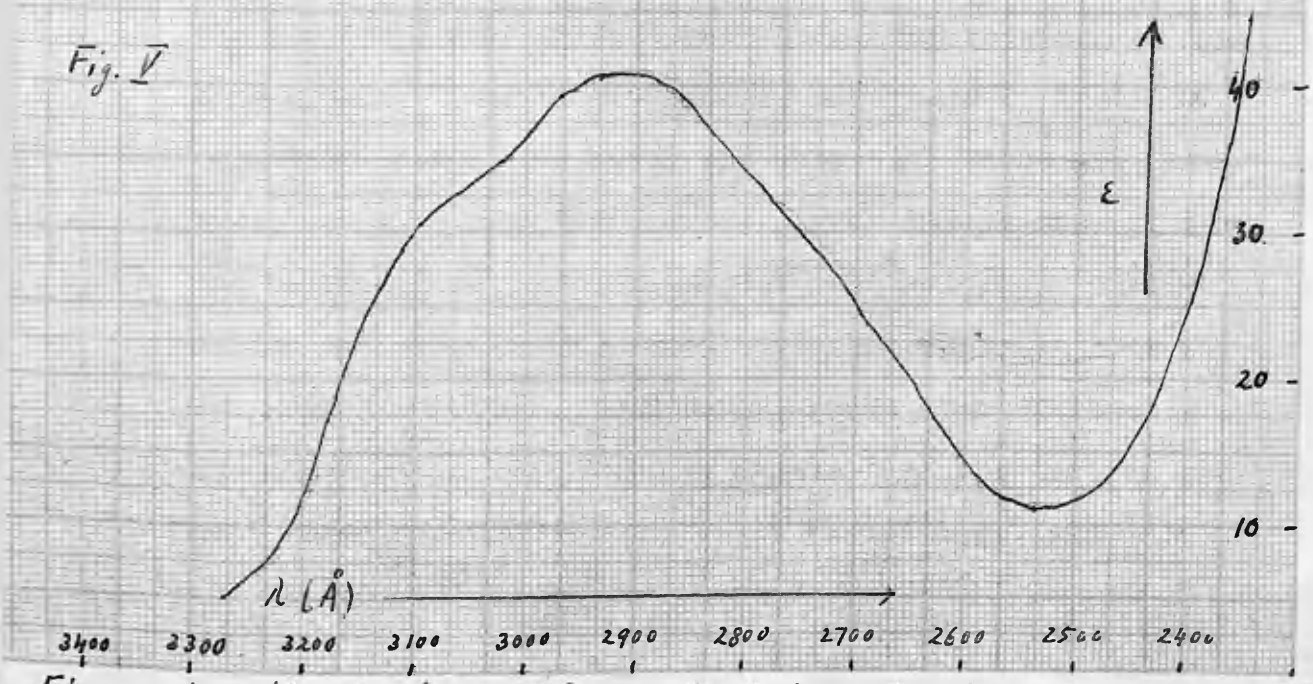


Fig. IV. Absorption Spectrum of Parasantonic Acid in Alcohol

Fig. V. Absorption Spectrum of Santonic Acid in Alcohol

$\varepsilon = 41$. The subsidiary band seems to have its maximum in the neighbourhood of $\lambda = 3100$ Å. The measurements, however, were not in this case sufficiently accurate so as to allow of conclusions based on details in the shape of the absorption curve: the curve was only recorded in order to assert the order of magnitude of the intensity of the band.

Santonine (Table VI, Fig.VI)

Although the absorption spectrum of santonine itself has been measured by Gomez (32), it was necessary to measure it anew since the results of the Spanish author were not accessible and the extinction of santonine in the ultra-violet is valuable for the discussion of the properties of the santonine derivatives. In Fig.VI $\log \varepsilon$ (not ε as in the other graphs) is plotted against the wave-lengths, so that both bands can be shown on the same graph. As in the case of the isomeric lactones described above, two bands are observed: there are, however, considerable differences. The intensities of the two bands are of different order of magnitude: their maxima are shifted towards the visible region: both bands are much more diffuse and consequently less distinct from one another. It is seen on Fig.VI that the band in the near ultra-violet has not even a definite maximum but

joins on so closely to the second band that there is no minimum separating them. The absorption starts in the visible (santonine is decomposed by light through the walls of glass vessels) and reaches $\varepsilon = 6$ at $\lambda = 3800$ Å, then the curve increases almost linearly up to $\varepsilon = 40.1$ at $\lambda = 3328$ Å. There is at this point a marked fall in the slope of the curve: the absorption remains almost constand down to $\lambda = 3031$ Å, $\varepsilon = 45.9$. This effect must be considered as caused by the ketonic absorption band in this region. Below $\lambda = 3031$ Å the absorption strongly increases up to a maximum of $\varepsilon = 9920$ at $\lambda = 2370$ Å. The spreading of the absorption towards the visible is probably due to the fact that in santonine the ketonic group is embedded in the conjugated system -CH=CH-CO-CH=CH-; it is known that conjugated double bonds tend to shift the absorption towards the long waves. As to the band which is assumed to be the lactonic one, it is noticed that it too spreads much further towards the visible than the analogous bands of the two other lactones and that it is much more intense. The fact that changes in the concentration cause breaks in the extinction curve (shown on the graph) indicates that in the case of santonine there is a dependence of the absorption coefficient on the concentration.

TABLE VI.

Absorption Spectrum of Santonine in Alcohol.

Solution a). 0.4294 g. in 100 cm^3.

λ(Å)	Sector reading	ε	log ε	λ(Å)	Sector reading	ε	log ε
3736	0.1	5.73	0.76	3019	0.9	51.5	1.71
3556	0.2	11.5	1.06	2997	1.0	57.3	1.76
3501	0.3	17.2	1.24	2995	1.1	63.0	1.80
3454	0.4	22.9	1.36	2985	1.2	68.8	1.84
3380	0.5	28.7	1.46	2976	1.3	74.5	1.87
3355	0.6	34.4	1.54	2970	1.4	80.2	1.90
3328	0.7	40.1	1,60	2967	1.5	86.0	1.93
3031	0.8	45.9	1.66				

Solution b). 0.1540 g. in 100 cm^3.

2957	0.5	96	1.98	2925	1.0	176	2.25
2947	0.6	112	2.05	2919	1.1	192	2.28
2944	0.7	128	2.11	2918	1.2	208	2.32
2934	0.8	144	2.16	2916	1.3	224	2.35
2927	0.9	160	2.20	2917	1.4	239	2.38

Solution c). 0.02976 g. in 1000 cm^3.

2558	0.9	7450	3.87	2360	1.2	9920	4.00
2503	1.0	8270	3.92	2319	1.1	9100	3.96
2449	1.1	9100	3.96	2305	1.0	8270	3.92
2377	1.2	9920	4.00	2283	0.9	7450	3.87
2919	0.1	827	2.92	2731	0.5	4130	3.62
2829	0.2	1650	3.22	2689	0.6	4960	3.70
2777	0.3	2480	3.39	2660	0.7	5780	3.76
2741	0.4	3310	3.52	2631	0.8	6610	3.82

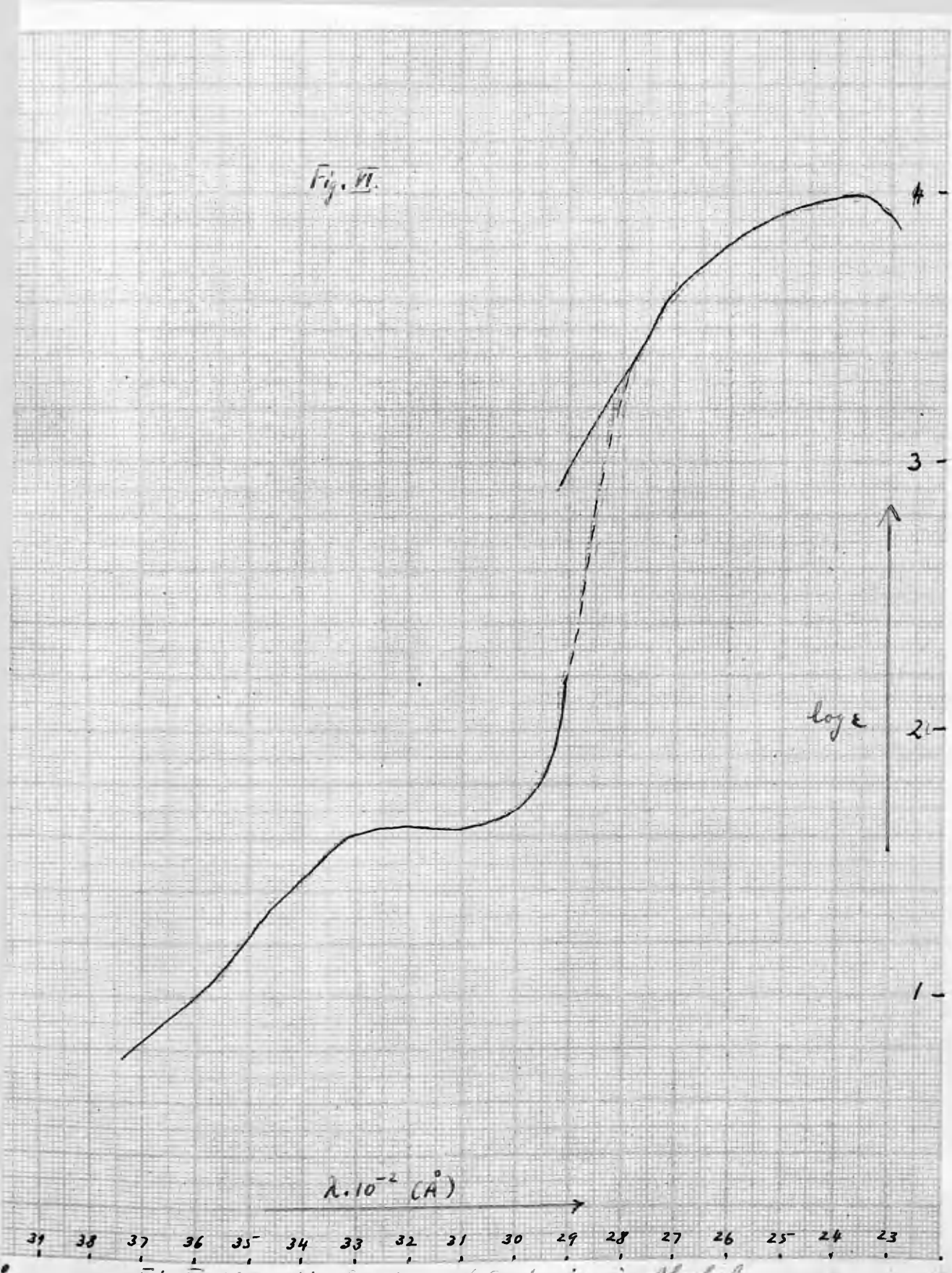


Fig. VI. Absorption Spectrum of Santonine in Alcohol.

TABLE VII.

Absorption Spectrum of l-Desmotroposantonine in Alcohol.

Solution a). 0.0092 g. in 100 cm^3.

λ (Å)	Sector read.	ε	λ (Å)	Sector read.	ε
3011	0.1	268	2737	0.4	1070
3005	0.2	535	2718	0.3	803
2995	0.3	803	2670	0.2	535
2988	0.4	1070	2621	0.1	268
2975	0.5	1340	2417	0.1	268
2968	0.6	1605	2402	0.2	535
2963	0.7	1870	2383	0.3	803
2944	0.8	2140	2377	0.4	1070
2923	0.9	2410	2372	0.5	1340
2809	0.9	2410	2361	0.6	1605
2788	0.8	2140	2357	0.7	1870
2774	0.7	1870	2349	0.8	2140
2767	0.6	1605	2344	0.9	2410
2749	0.5	1340			

Solution b). 0.0046 g. in 100 cm^3.

2998	0.2	1070	2341	0.6	3210
2964	0.3	1605	2332	0.7	3840
2946	0.4	2140	2324	0.8	4280
2824	0.4	2140	2314	0.9	4810
2774	0.3	1605	2312	1.0	5350
2715	0.2	1070	2304	1.1	5880
2400	0.2	1070	2298	1.2	6420
2378	0.3	1605	2288	1.3	6950
2362	0.4	2140	2273	1.4	7490
2350	0.5	2675	2242	1.5	8020

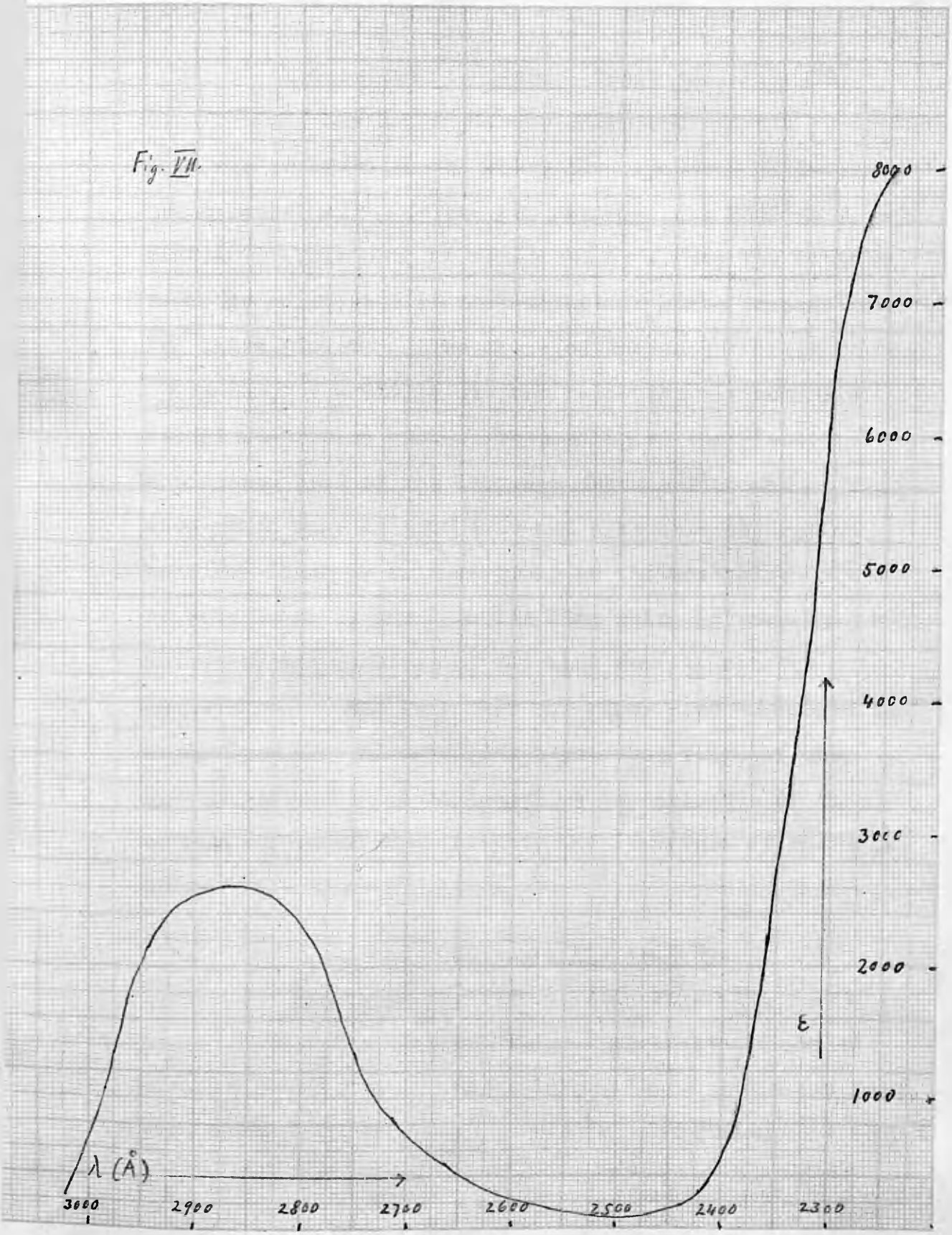


Fig. VII. Absorption Spectrum of l-Desmotroposantonine in Alcohol.

l-Desmotroposantonine (Table VII, Fig.VII)

Only one comparatively sharp and intense absorption band was observed in the absorption spectrum of l-desmotroposantonine. It has its maximum $\varepsilon = 2500$ at $\lambda = 2865$ Å. This band is separated by a very low minimum from the rapid rise of the extinction curve towards the far ultra-violet. The shape of the curve indicates that $\varepsilon = 8020$ $\lambda = 2241$ Å is just below the maximum of a second absorption band corresponding to the "lactonic" absorption band of the lactones described above. The absorption band at 2865 Å is not a ketonic absorption band for there is no $-\overset{|}{C}=O$ group in the molecule. It must be attributed to the phenolic ring which is present: both intensity and position of the band seem to confirm this assumption. The fact that the other band has moved towards the short wave-lengths beyond the range of the spectrophotometer is explained by the presence of the aromatic ring which stabilises the structure of the molecule.

B). Rotatory Dispersions.

Parasantonide (Table VIII, Figs.VIII & IX)

The rotatory dispersion of parasantonide in the visible has been measured by Nasini (33). His results are included in Fig.VIII, in the region between $\lambda = 6870$ Å

TABLE VIII.

Rotatory Dispersion of Parasantonide in the Ultra-Violet in Alcohol.

Solution a). 0.3232 g. in 100 cm^3. l = 1 cm.

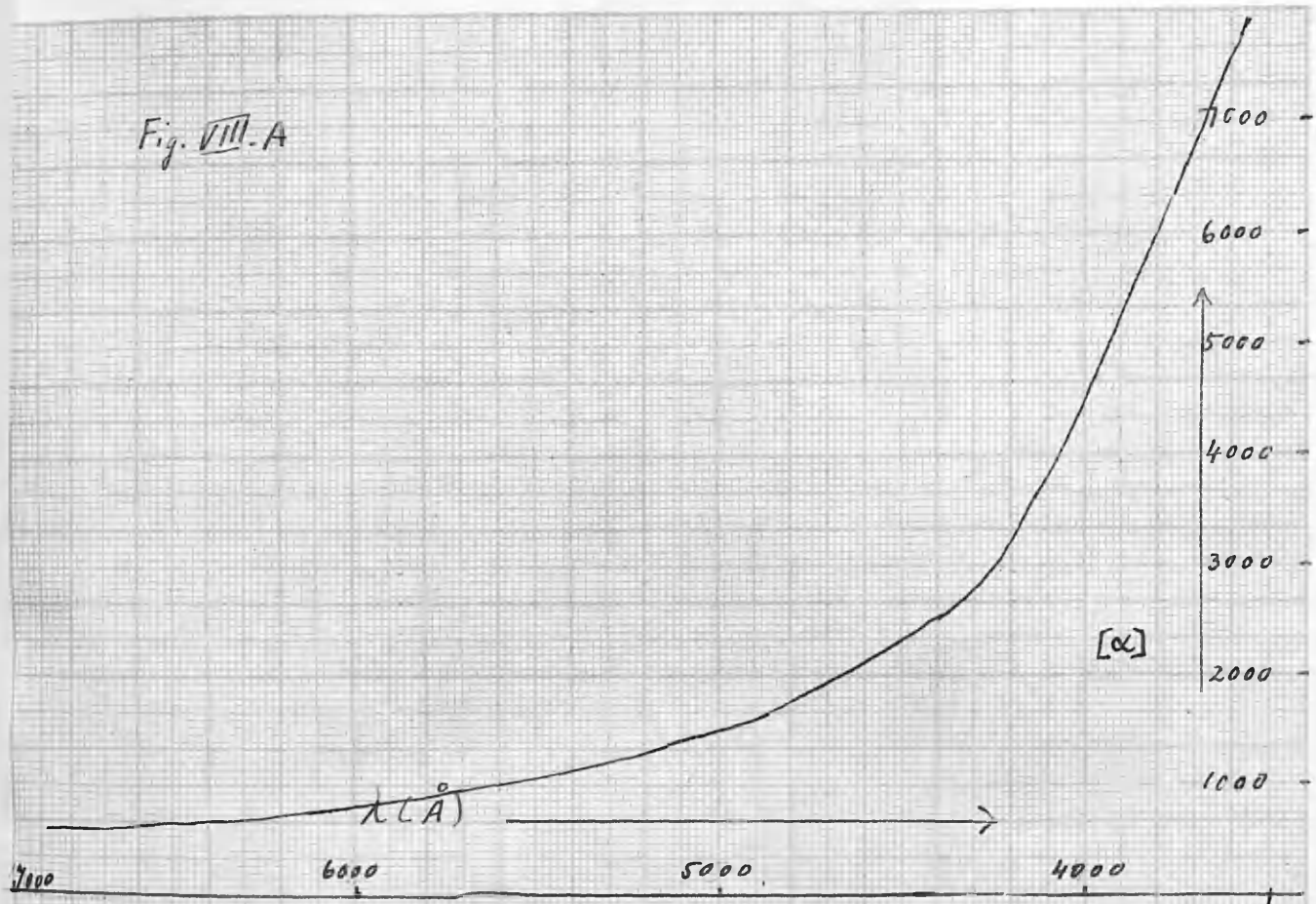
λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
4063	1.30°	4022°	3647	2.30°	7116°
4034	1.50	4641	3575	2.50	7734
3920	1.70	5260	3521	2.70	8354
3719	2.10	6497	3485	3.10	9592

Solution b). 0.0453 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
3350	0.70°	15500°	3193	1.40°	31090°
3262	1.10	24430	3178	1.35	29980
3257	1.30	28870	3172	1.30	28870
3248	1.35	29980	3117	1.10	24430
3234	1.40	31090	3059	0.70	15550

Solution c). 0.0324 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
3042	0.45°	13890°	2859	-1.05°	-32400°
2941	-0.35	-10800	2846	-1.10	-33950
2902	-0.75	-23150	2699	-1.10	-33950
2899	-0.85	-26230	2631	-1.05	-32400
2878	-0.95	-29320	2575	-0.95	-29320



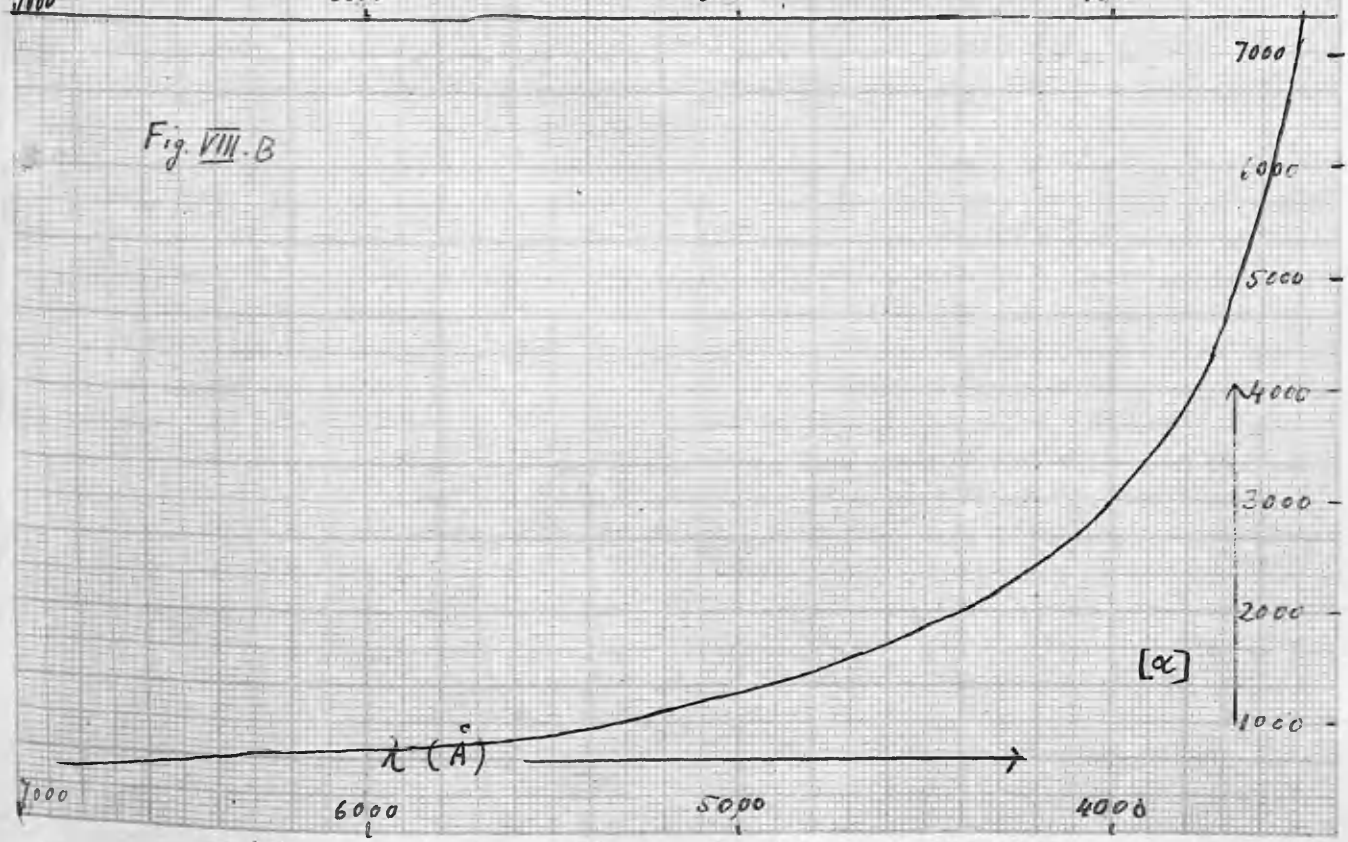


Fig. VIII A) Rotatory Dispersion of Parasantonide in the Visible.
B) Rotatory Dispersion of Santonide in the Visible.

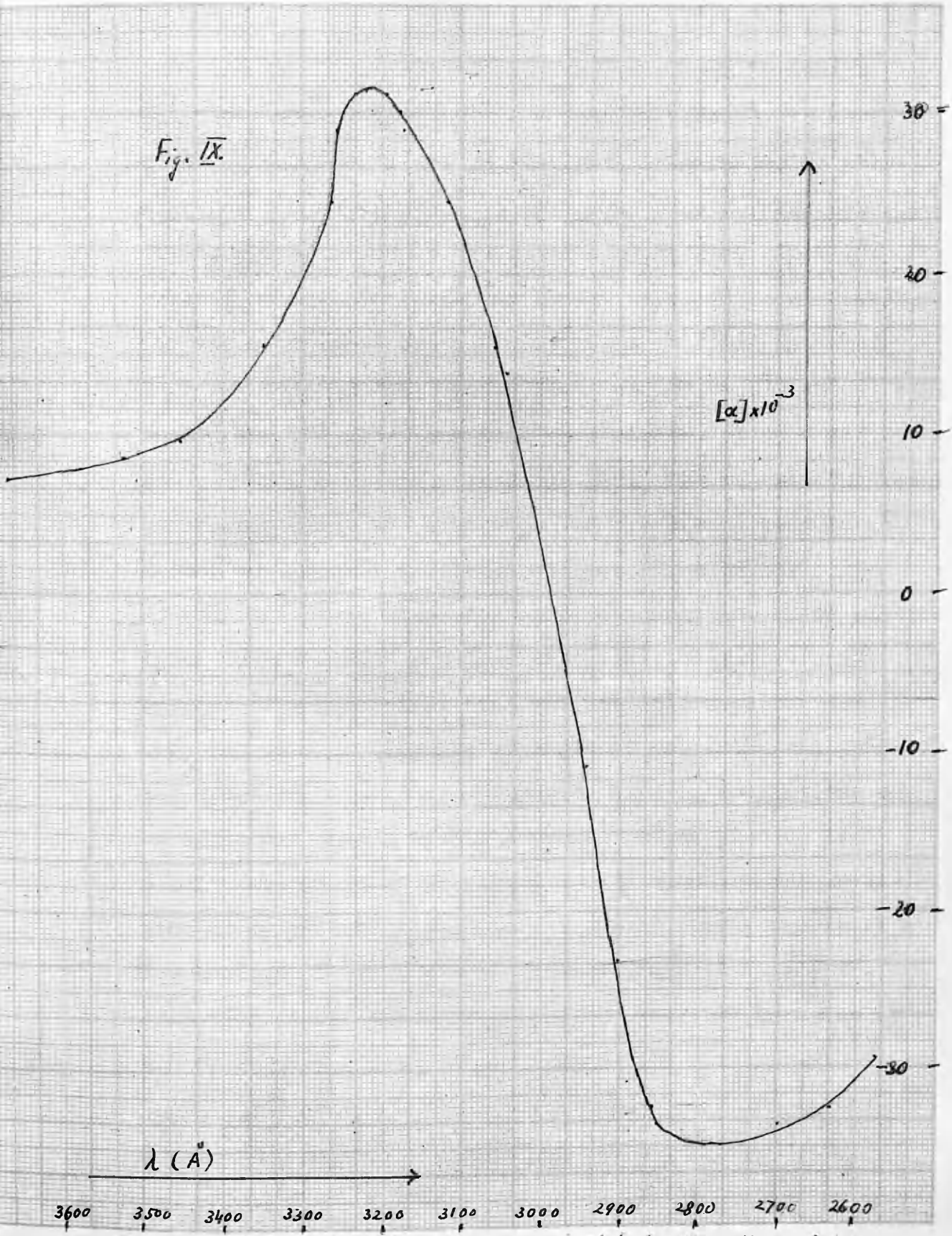


Fig. IX. Rotatory Dispersion of Parasantonide in the Ultra-Violet.

and 4226 Å. The dispersion curve recorded by Nasini (in $CHCl_3$ solution) is seen to join on smoothly to the curve obtained with the ultra-violet polarimeter in solutions of the substance in alcohol. Fig. IX shows the rotatory dispersion in the ultra-violet; the slope increases steadily and becomes almost vertical before reaching the maximum of $[\alpha] = 32{,}000^\circ$ at $\lambda = /3210$ Å; there is a reversal of sign of the rotation ($[\alpha] = 0^\circ$) at = 2980 Å and the rotations fall to a minimum of $[\alpha] = -35{,}000^\circ$ at $\lambda = 2750$ Å. The readings could not be extended beyond this region since the absorption of the second band is too strong to transmit sufficient light; even in the region of the first band exposures up to one hour had to be given owing to the small transparency of the substance. It appears from Table VIII that the specific rotation does not vary appreciably with the strength of the solution; all the specific rotations measured in different solutions can be collected into a smooth curve. Parasantonide is slowly decomposed by the light of the iron-arc (the rotation of an alcoholic solution decreases in the course of a few hours); it was, therefore, necessary to supply the cell with fresh solutions during the exposure by means of the arrangement described on p. 24 .

The rotatory dispersion of parasantonide in the ultra-violet is a striking example of a Cotton-effect

TABLE IX.

Rotatory Dispersion of Santonide in the Ultra-Violet in Alcohol.

Solution a). 0.4030 g. in 100 cm^3. l = 1 cm.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
3924	1.20°	2978°	3555	2.80°	6949°
3776	1.60	3970	3451	3.60	8933
3660	2.00	4963	3360	5.20	12900

Solution b). 0.0416 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
3307	0.65°	15630°	3100	0.85°	20430°
3292	0.75	18030	3075	0.75	18030
3274	0.85	20430	3059	0.65	15630
3263	0.90	21630	3000	0.05	1230
3262	0.95	22830	2957	-0.45	-10800
3248	1.00	24040	2807	-1.20	-28850
3158	1.00	24040	2782	-1.25	-30050
3148	0.95	22820	2719	-1.25	-30050
3126	0.90	21630			

Solution c). 0.0340 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
2945	-0.40°	-11770°	2864	-0.80°	-23540°
2895	-0.70	-20590	2644	-0.90	-26470

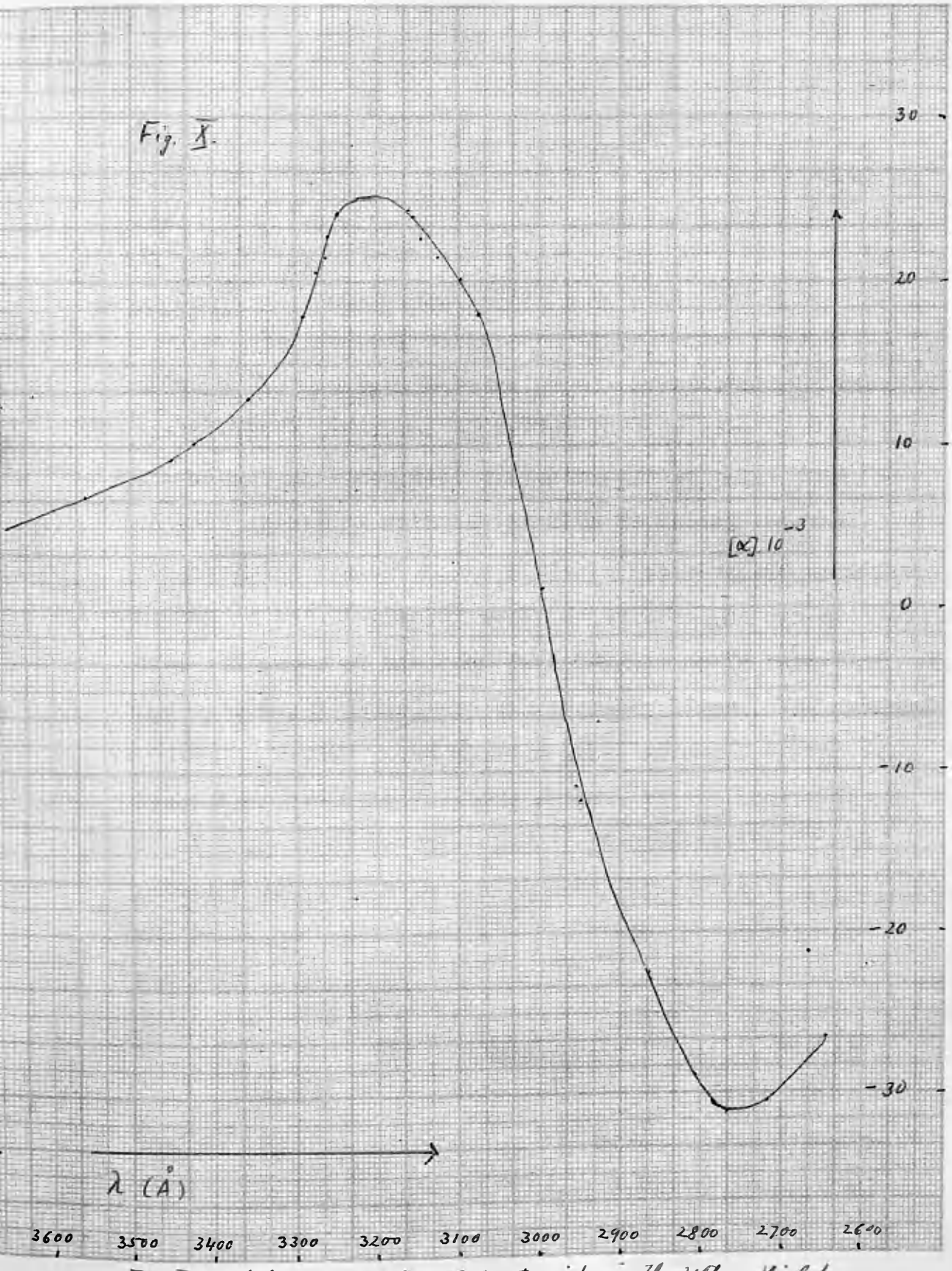


Fig. X. Rotatory Dispersion of Santonide in the Ultra-Violet.

connected with the absorption band at λ = 2980 Å. The maxima and minima of the curve represent the highest specific rotations measured in homogeneous solution up to now.

Santonide (Table IX, Figs. VIII & X)

The rotatory dispersion of santonide resembles closely the rotatory dispersion of parasantonide; the visible part (measured by Nasini (33) is seen on Fig.VIII). The values measured with the ultra-violet polarimeter are in good agreement with the results of Nasini for the neighbouring region in the blue. Positive and negative maxima of the dispersion curve as well as the reversal of sign all occur at the same wave-lengths as in parasantonide. The extrema, however, are considerably lower: the maximum $[\alpha]$ = 25,000°, the minimum $[\alpha]$ = -31,000°. The very steep fall from the positive maximum to the longer waves is also observed in this case. The variation of the specific rotation with the concentration is not appreciable. The readings taken for the region near the visible are recorded in Fig.VIII.

Parasantonide-imide (Table X, Fig.XI)

The transparency of parasantonide-imide being much smaller than the transparency of the two foregoing substances (see p.35), the rotatory dispersion could not be

measured to the same degree of accuracy. The readings, however, are sufficiently reliable to ascertain that the negative maximum with $[\alpha]$ = 51,000° λ = 2800 Å strongly exceeds the corresponding value of parasantonide. The reversal of sign is at λ = 3110 Å (the maximum of the absorption band occurs at λ = 3065 Å) and the positive maximum $[\alpha]$ 34,000 at λ = 3280 Å. The fall of the dispersion curve towards the visible was not measured since the substance is not easily prepared in quantities as required to make up strong solutions (as would be necessary for the regions of smaller rotation) and as it was thought - by analogy with the curves of santonide and parasantonide - that these regions would not be of any particular interest. The same applies to measurements in the visible region. ($[\alpha]$ = 1135° at λ = 5893 Å.)

Santonine, Parasantonic Acid, Santonic Acid, Hydrosantonide and l-Desmotroposantonine.

Although the absorption in the region about λ = 3000 Å in the first three compounds is much weaker than in the lactones described above, the rotatory dispersion could not be recorded in the absorbing regions since the rotations are too small to be measured through the bands.

The rotatory dispersion of hydrosantonide was measured in the visible in order to find out whether this

TABLE X.

Rotatory Dispersion of Parasantonide-imide in Alcohol.

Solution a). 0.0187 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ	α	$[\alpha]$
3381	0.55°	29400°	3212	0.55°	29400°
2788	-0.95	-50800	2807	-0.95	-50800

Solution b). 0.0140 g. in 100 cm^3.

λ (Å)	α	$[\alpha]$	λ	α	$[\alpha]$
3345	0.45°	32200°	3034	-0.25°	-17900°
3218	0.45	32200	2740	-0.65	-46500
2912	-0.55	-39400			

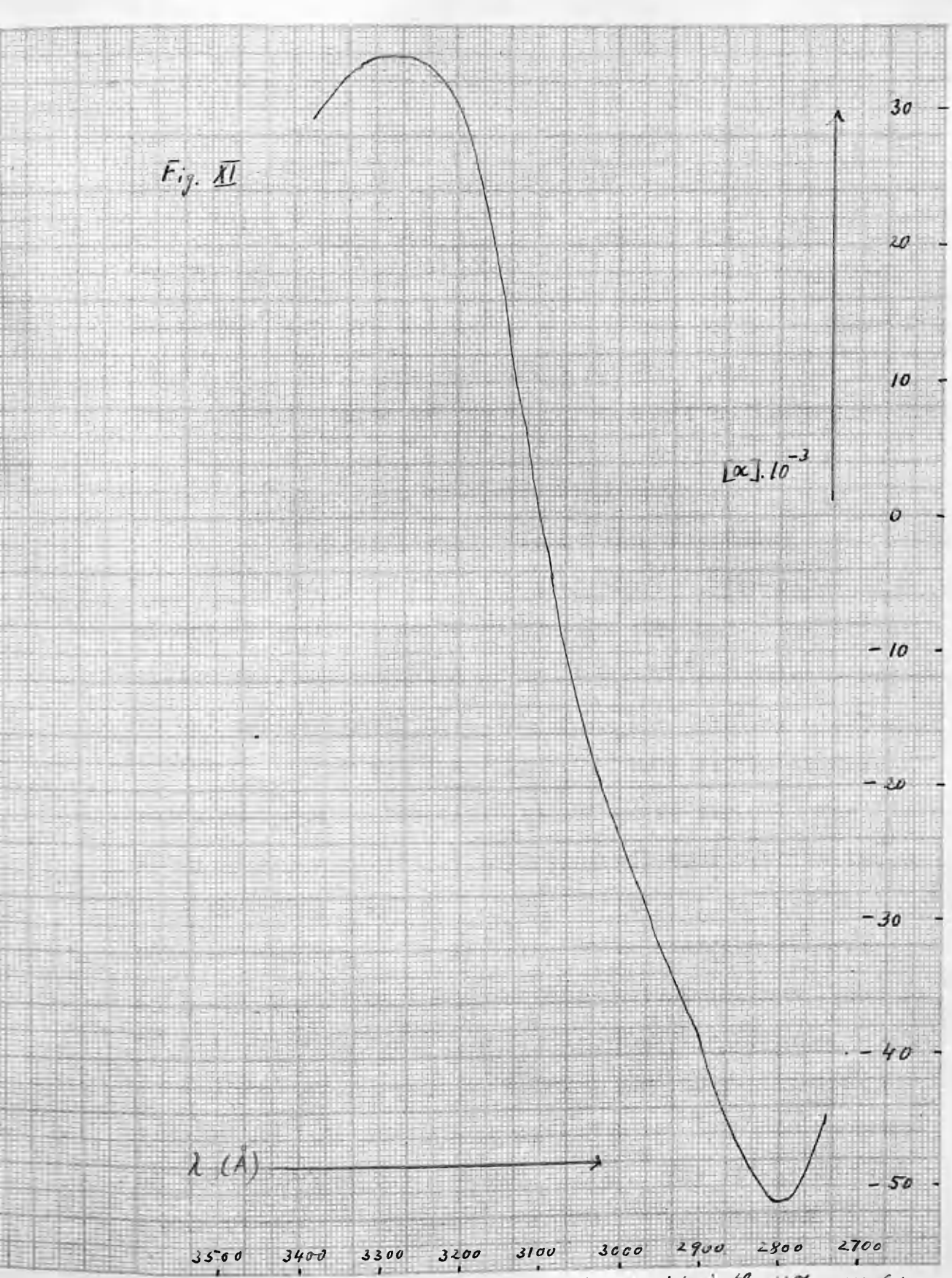


Fig. XI. Rotatory Dispersion of Parasantonide-imide in the Ultra-Violet.

lactone belongs to the strongly rotating compounds of the santonine group: this is not the case as $[\alpha]_D = 258^\circ$, $[\alpha]_{5600\text{Å}} = 290^\circ$. No attempt was therefore made to measure the rotatory dispersion in the ultra-violet.

The rotatory dispersion of l-desmotroposantonine increases from $[\alpha] = 101.5^\circ$, $\lambda = 6800$ Å to $[\alpha] = 201.5^\circ$, at $\lambda = 5100$ Å. The absorption in the ultra-violet is too strong to allow ~~of~~ the measurement of the rotation.

Circular Dichroism.

Parasantonide (Table XI, Fig.XII)

In spite of the strong absorption, the circular dichroism could be measured through the band: the ellipticity readings amounted up to $\alpha = 1.50^\circ$. This is due to the exceptionally high values of the circular dichroism $(\varepsilon_\ell - \varepsilon_r)_{max} = 36.8$ at $\lambda = 3020$ Å. This is the highest value measured in isotropic solutions so far. The curve is not symmetrical but rather steeper towards the long wave-length side. It is interesting to note that here the difference of the absorption coefficients for left-handed and right-handed circularly polarised light is of the same magnitude as the absorption coefficient ($\varepsilon = \frac{\varepsilon_\ell + \varepsilon_r}{2}$) of an ordinary ketonic band (e.g., acetone or camphor). The anisotropy factor $g = \frac{\varepsilon_\ell - \varepsilon_r}{\varepsilon}$ is recorded in the fifth ~~and tenth~~ column of Table XI: it is not constant throughout the band as it should be - according to

TABLE XI.

Circular Dichroism and Anisotropy Factor of Parasantonide in Alcohol.

0.0323 g. in 100 cm^3.

λ (Å)	α	$\varepsilon_l - \varepsilon_r$	ε	$\frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$
3257	0.40°	9.2		
3234	0.60	13.9	280	0.050
3205	0.80	18.5	410	0.045
3175	1.00	23.1	610	0.038
3148	1.20	27.7	735	0.038
3100	1.40	32.3	885	0.037
3091	1.50	34.6	935	0.037
2941	1.50	34.6	1140	0.030
2892	1.40	32.3	975	0.033
2846	1.20	27.7	820	0.034
2762	1.00	23.1	560	0.041
2706	0.80	18.5	439	0.042
2642	0.60	13.9	382	0.036

Fig. XII

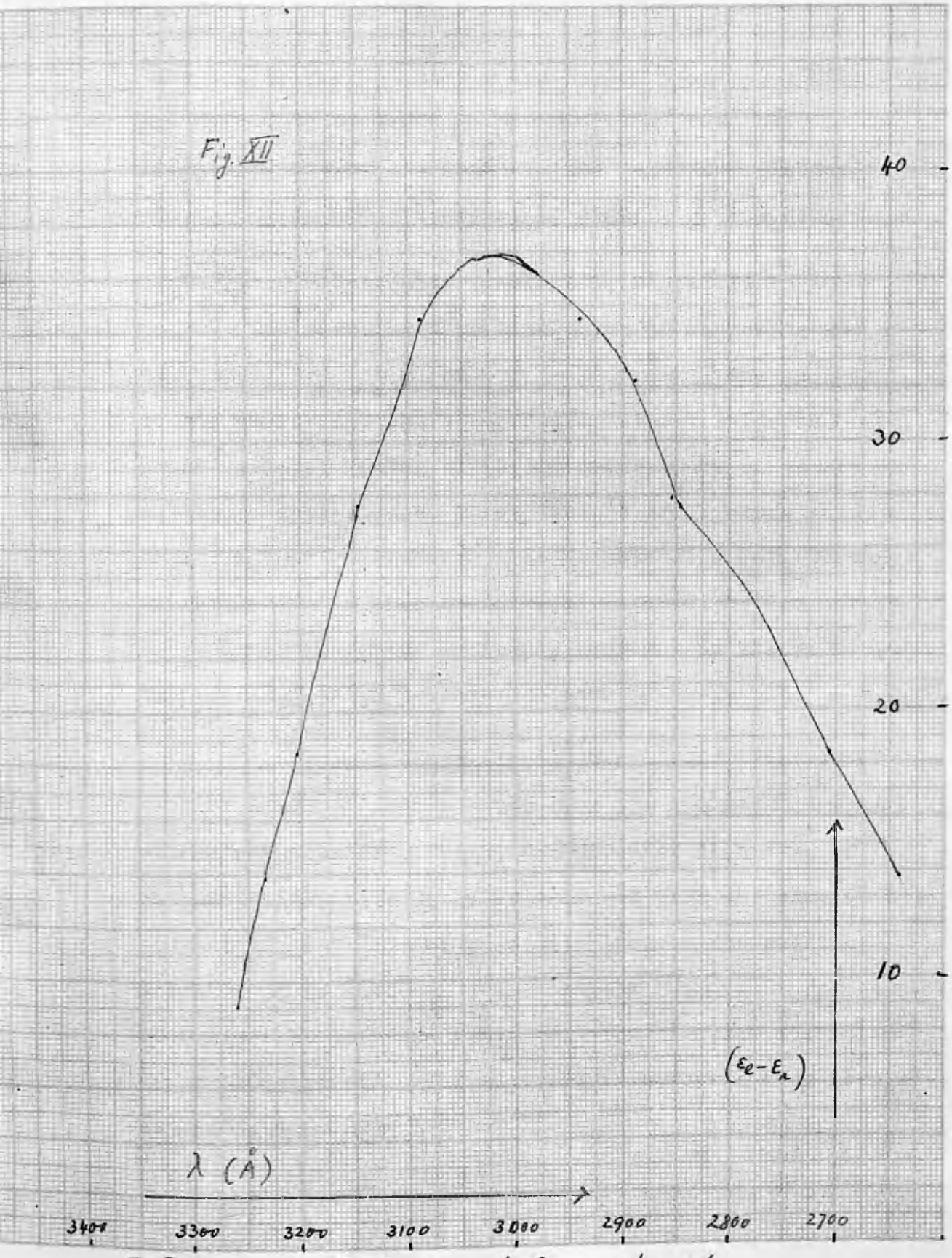


Fig. XIII. Circular Dichroism of Parasantonide.

Kuhn's theory - for simple absorption bands. While being approximately constant in the middle of the band, it is irregular towards its edges. The anisotropy-factor is strong though not exceptionally high. $\bar{g} = 0.037$.

Santonide (Table XII, Fig.XIII)

The circular dichroism curve of santonide has a maximum $(\varepsilon_e - \varepsilon_r)_{max} = 27$ at $\lambda = 3000$ Å. The band is rather narrow and the steeper side lies towards the far ultra-violet. Owing to its narrowness the curve cannot easily be approximated to by Gauss's error curve $(\varepsilon_e - \varepsilon_r) = (\varepsilon_e - \varepsilon_r)_{max} \times e^{-\left(\frac{\lambda-\lambda_e}{\Theta}\right)^2}$ although this formula is a satisfactory approximation to most measured circular dichroism curves. The anisotropy-factor is fairly constant in the middle of the band but falls towards the short wave-lengths $\bar{g} = 0.03$.

Parasantonide-imide (Table XIII, Fig.XIV)

Although this was not true for the measurements of the rotatory dispersion, the circular dichroism of parasantonide-imide could be measured with the same accuracy as that of santonide or parasantonide. The readings amounted up to 1.25°. The maximum $\varepsilon_e - \varepsilon_r = 58$ for $\lambda = 3040$ Å. It is even higher than the circular dichroism of parasantonide. The anisotropy factor is very irregular, as can be seen from Table XIII.

TABLE XII.

Circular Dichroism and Anisotropy Factor of Santonide in Alcohol.

0.0416 g. in 100 cm^3.

λ (Å)	α	$\varepsilon_e - \varepsilon_r$	ε	$\frac{\varepsilon_e - \varepsilon_r}{\varepsilon}$
3222	0.35°	6.3	200	0.032
3197	0.55	9.9	310	0.032
3178	0.85	15.2	405	0.038
3162	0.95	17.0	472	0.035
3134	1.05	18.8	565	0.033
3100	1.25	22.4	670	0.033
3083	1.35	24.2	755	0.032
2912	1.35	24.2	861	0.028
2874	1.25	22.4	760	0.030
2859	1.05	18.8	705	0.027
2852	0.95	17.0	680	0.025
2846	0.85	15.2	660	0.023
2826	0.55	9.9	590	0.017

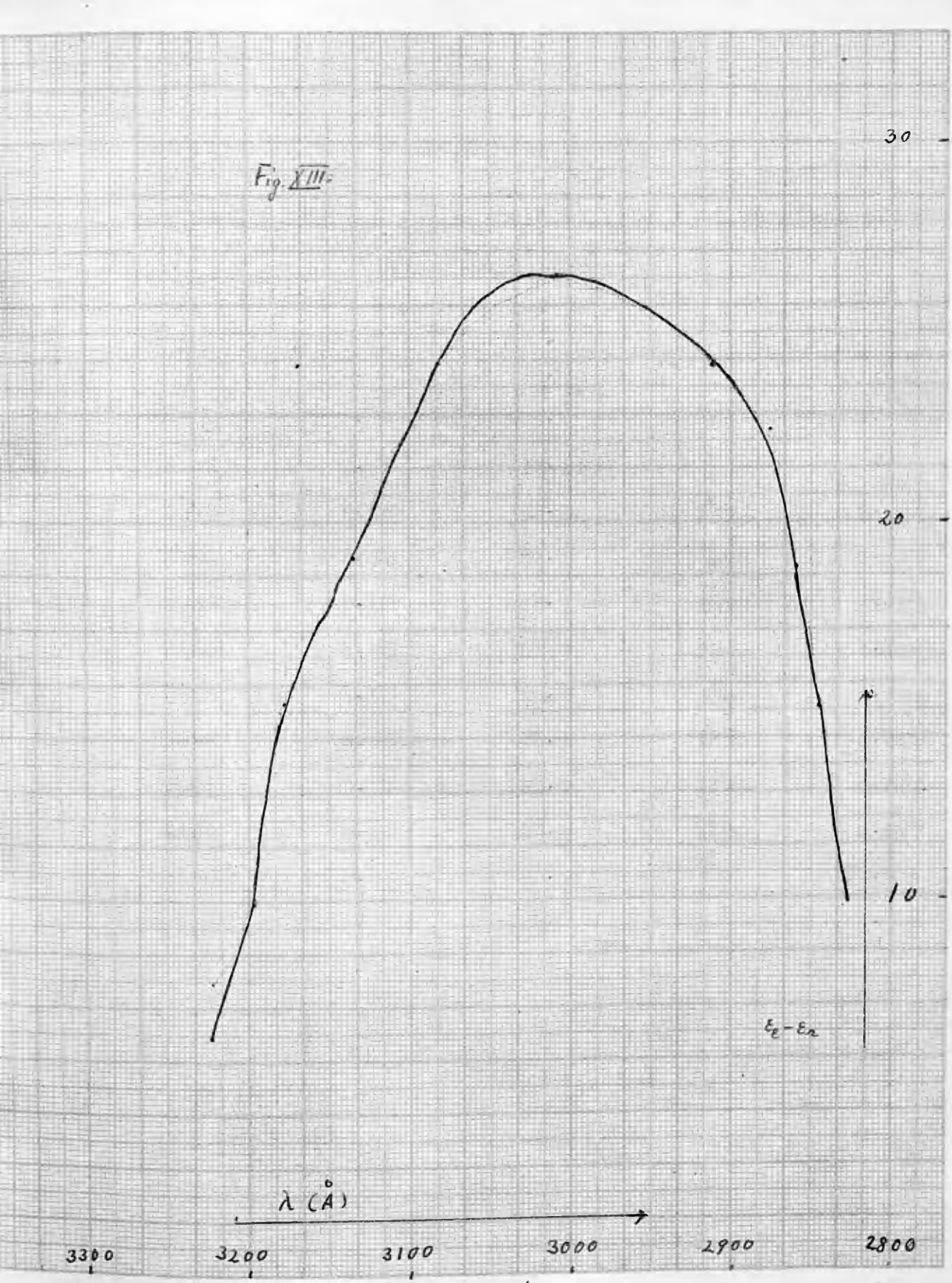


Fig. XIII. Circular Dichroism of Santonide.

TABLE XIII.

Circular Dichroism and Anisotropy Factor of Parasantonide-imide in Alcohol.

0.0140 in 100 cm^3.

λ (Å)	α	$\varepsilon_\ell - \varepsilon_r$	ε	$\frac{\varepsilon_\ell - \varepsilon_r}{\varepsilon}$
3345	0.25°	13.25		
3325	0.45	23.8	470	0.051
3292	0.65	35.0	520	0.067
3235	0.85	45.1	1620	0.028
3100	1.05	55.7	2800	0.020
2953	1.05	55.7	2360	0.025
2892	0.85	45.1	1630	0.028
2828	0.65	35.0	1220	0.029
2731	0.45	23.8	1380	0.017

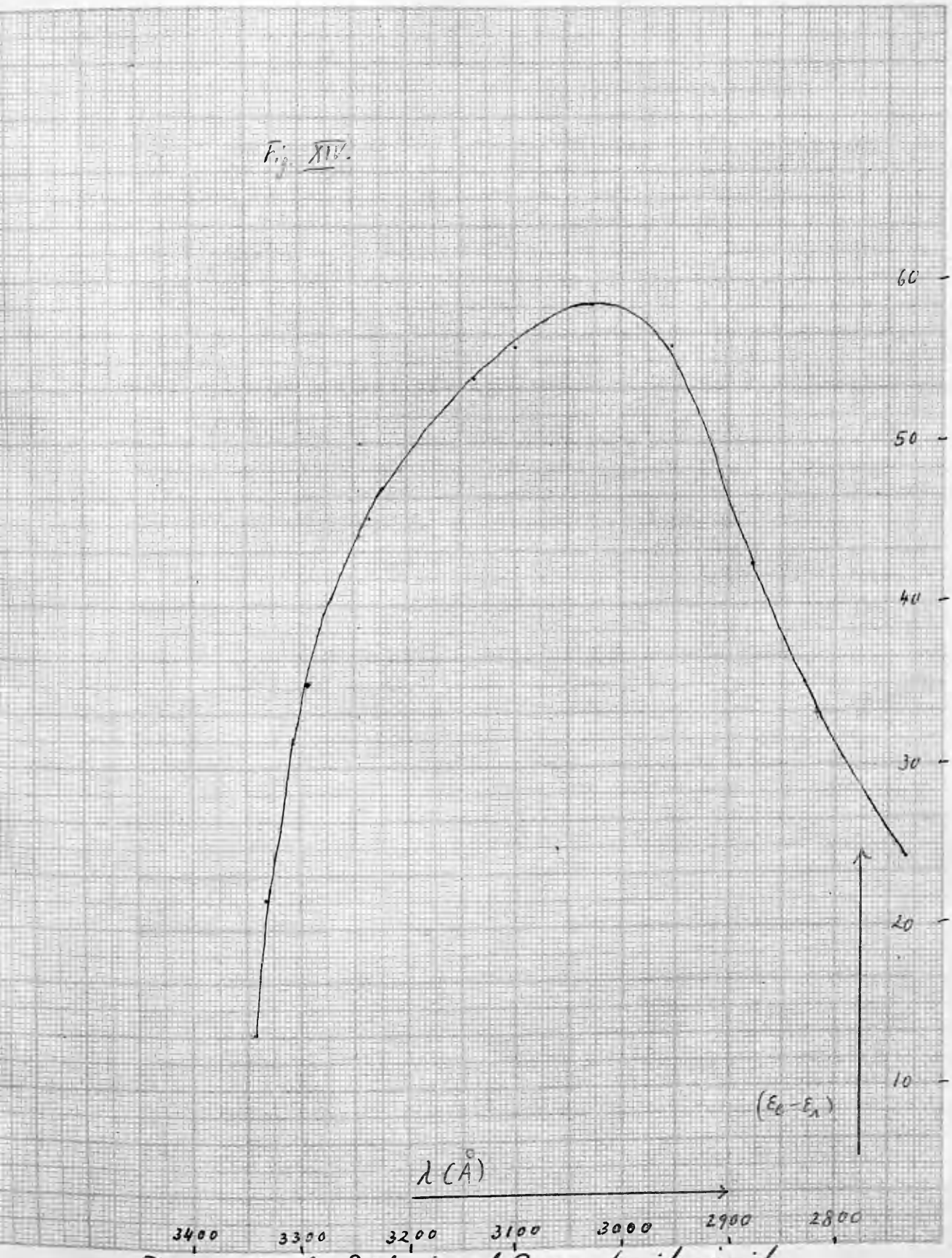


Fig. XIV. Circular Dichroism of Parasantonide-imide.

The Chemistry of the Santonine Group.

In order to be able to discuss the optical properties of santonine and some of its derivatives, a short summary of their chemical properties and constitution - as far as it is known - will be useful.

Most of the work on the chemistry of santonine and its derivatives has been carried out by Cannizzarro and his pupils in the second half of last century. Although these Italian authors were not able to establish the correct formula of santonine and santonic acid, their thorough research on the properties and transmutations of the many derivatives of santonine was fundamental for the later investigations in this field. The discovery of the unusually elevated rotations of some of the compounds of the group is also due to them.

Various formulae have been suggested for santonine by Cannizzarro and Gucci (34), Francesconi (35), Wedekind (36) and others. But it was only in 1930 that Clemo, Haworth and Walton (37) and Clemo and Haworth (38) succeeded in proving a formula agreeing with all chemical properties of santonine (I). It is a keto-lactone derived from tetrahydronaphthalene. Santonine forms an oxime when treated with hydroxylamine hydrochloride. Action of acid transforms it into desmotroposantonine (II): there is a tendency on the part of the

CH=CH-CO-CH=CH to change over to the enolic form which involves the change to the stable aromatic structure of the unsaturated ring. Acted on by alkali santonine forms santoninic acid (III), the hydroxy acid corresponding to the lactone. The acid is unstable in neutral and acid solutions where santonine is formed spontaneously. Prolonged heating with alkali causes migration of the double bonds and gives rise to the formation of santonic acid (IV): from the latter, santonine cannot be recovered. It is a diketo-carboxylic acid and gives - according to the conditions - a monoxime or a dioxime by the action of concentrated sulphuric acid - a lactone - metasantonide - is obtained to which formula (VI) was assigned (39). Proof for it is the fact that it can be reduced (Zn + acid) to the lactone hydrosantonide which is identical with the lactone obtained from hydrosantonic acid (which is formed by the reduction of santonic acid with sodium amalgam.) When santonine is reduced under the same conditions as metasantonide, desmotroposantonous acid is formed (VIII). Metasantonide forms an oxime and - acted on by acetic anhydride - it gives an acetyl derivative. The hydroxy acid corresponding to metasantonide is not santonic acid but metasantonic acid which is a stereoisomeride of the former (V). Other ways to prepare metasantonic acid are the oxydation of hydrosantonide with Ag_2O and opening the lactone ring on heating

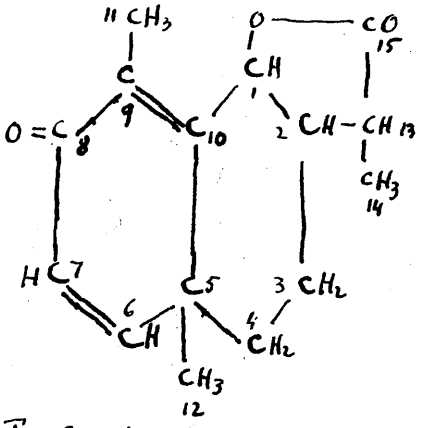
santonic acid with acetic acid to 260-300°. These facts confirm the assumption of Francesconi that the only difference between santonic and metasantonic acid is the position of the side chain with respect to the plane of the ring. The mono- and dioximeas well as the mono- and diacetyl derivatives of metasantonic acid are known. The monoacetyl compound is insoluble in alkali carbonate solution and does not form an oxime: this led Francesconi (39) to suggest for it the formula (IX). Analogous formulae were suggested for the chloride and the bromide of the acid because of their insolubility in alkali carbonate solutions.

When santonic acid is dissolved in glacial acetic acid and - after distilling off the solvent - heated to 180°, santonide is formed: the same procedure, when applied to metasantonic acid, gives rise to the formation of parasantonide. In this case the temperature has to be higher. Parasantonide is also obtained from santonic acid when the latter is heated (after treatment with CH_3COOH) to 260-300° owing to the transformation of santonic acid into metasantonic acid at this temperature. Both santonide and parasantonide are lactones of very similar properties. The hydroxy acids corresponding to them are not the acids from which they are prepared but isosantonic

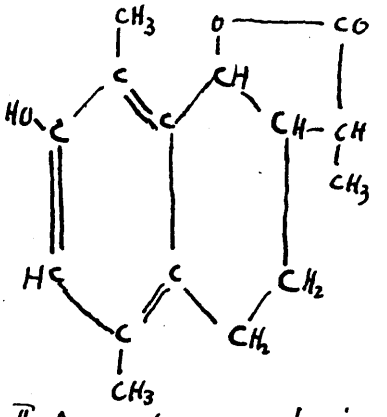
and parasantonic acids: they are isomers of santonic acid. They do not, however, form oximes or acetyl derivatives. Acetic anhydride transforms them into the lactones and does not act on their esters. The change from acid to lactone and vice versâ does not take place as readily as with santonine and santoninic acid. While acetic anhydride is necessary to transform the acid into the lactone, warming with concentrated HCl or alkali is required for the reverse reaction. Treatment with zinc and acetic acid changes parasantonide into parasantonic acid instead of reducing it (see metasantonide). From all these properties it appears that santonide and parasantonide must have a constitution different from santonine or metasantonide. The fact that neither lactone nor hydroxy acid forms an oxime with hydroxylamine hydrochloride (the lactone adds 1 molecule NH_2OH) suggests the absence of the distant ketonic CO group as present in santonine in position 8. The chemical inertness of the other CO group present in santonic acid can be explained by steric hindrance: the fact that no reduction is effected by nascent hydrogen excludes for the lactones the double bond between the C-atoms 1 and 2. The only alternative is the closure of the lactone ring to the C-atom 8 after the enolisation of the CO group. This enolisation may be made permanent by a migration of the double bond at the high temperature.

of the reaction so that the hydroxy acids have no CO group which could form an oxime. This does not agree, however, with Francesconi's observation that acetic anhydride does not react with the esters of parasantonic acid. The latter fact also excludes the possibility of an aromatic structure like desmotroposantonine since in that case, the phenolic, OH would give rise to the formation of an acetyl derivative (such a derivative of desmotroposantonine is known). There is, however, the possibility of a migration of the double bond Δ 9-10 to Δ 10-5 with a simultaneous migration of the methyl group from 5 to 6 which also takes place in the santonine-desmotroposantonine rearrangement. In this case the fact that an oxime is not formed could be explained by steric hindrance of the CO in 8. Parasantonide reacts with ammonia, splitting off 1 molecule H_2O. Parasantonide-imide does not, however, show the properties characteristic for ketone-imides: it is stable even to concentrated HCl and to alkali carbonates in the cold. When the NH_3 is split off the lactone ring is opened at the same time and parasantonic acid is formed. The same is true for the splitting off of NH_2OH in the addition compound of parasantonide and NH_2OH. Steric hindrance of the C=NH group seems to offer the explanation for this behaviour.

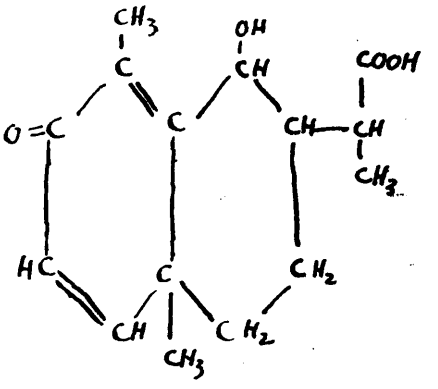
Santonine and Some Derivatives.



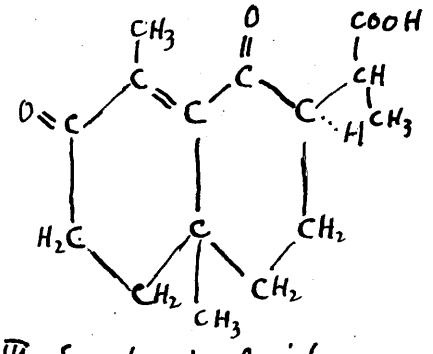
I. Santonine



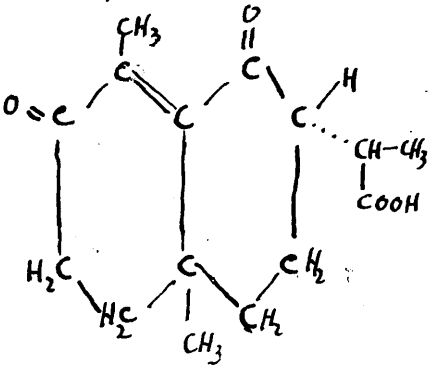
II. Desmotroposantonine



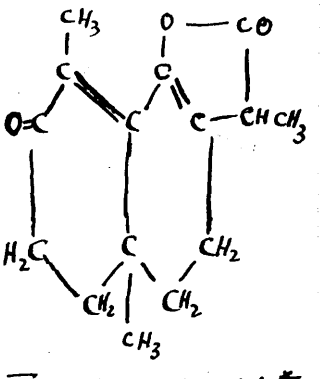
III. Santoninic Acid



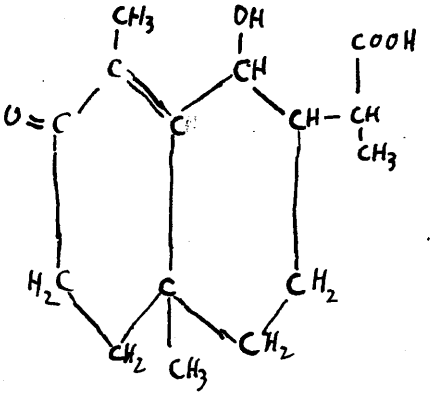
IV. Santonic Acid



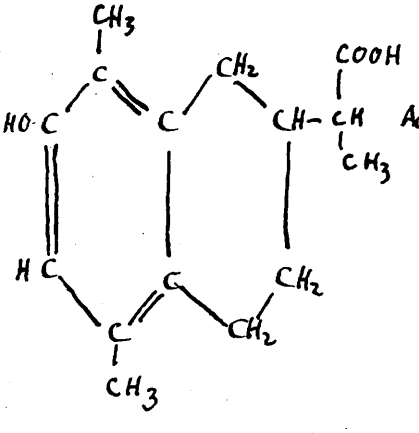
V. Metasantonic Acid.



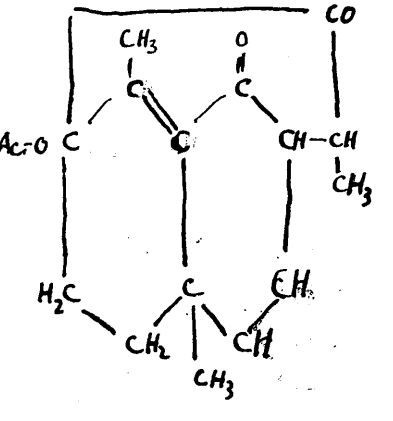
VI. Metasantonide*



VII. Hydrosantonic Acid



VIII. Desmotroposantonous Acid



IX. Acetyl-Metasantonic Acid*

* Francesconi's formulae are modified according to recent evidence. (37, 38)

Discussion.

A). Absorption Spectra.

The absorption spectra of santonide and parasantonide differ considerably from those of santonine and the acids of the group. In none of the other compounds was the intense absorption band at about λ = 3000 Å observed except 1-desmotroposantonine, where an intense band is found about the maximum at λ = 2940 Å. The other substances show a weak absorption band near λ = 3000 Å, which, by its intensity and its wave-length, must be attributed to the ketonic >CO: For the two strongly rotating lactones there are four alternatives: 1) the band in question is caused by a ketonic group which under the influence of neighbouring substituents is strongly intensified compared with ordinary ketonic bands: 2) the band is due to some other group present in parasantonide and santonide but absent in the other compounds. Aromatic structure which at first sight might seem to offer the explanation is unlikely for reasons derived from chemical evidence (p.49). A further fact against this assumption is the disappearance of the strong band when the lactone is transformed into the hydroxy acid: 3) the absorption is attributed to the lactone ring: or 4) to one of the carbon skeletons in the molecule. Assumption 3)

must be dropped for measurements on simpler lactones have shown that the absorption of the lactone group must be expected to lie at the far end of the ultra-violet region (see below, camphonolactone and β-butyro and γ-valerolactone). Assumption 4) is improbable for the band loses almost all its intensity when the lactone ring is opened. Such a fundamental change should not be expected to take place in the absorption of C-skeletons. Moreover the absorption of carbon skeletons with isolated double bonds usually lies at shorter wave-lengths. It is thus necessary to return to the first of the alternatives and consider the band as due to a $\backslash CO$ group. Similar cases where the absorption is strongly increased owing to the presence of other absorbing groups near a $\backslash CO$ group have been observed: thus diosphenol with the chromophoric group $-C = \overset{OH}{C} - \overset{O}{C}-$ has a maximum of $\varepsilon = 10^4$ at $\lambda = 2725$ Å and acetyl acetone has an absorption of $\varepsilon_{max} = 9450$ at $\lambda = 2730$ Å (40).

The second absorption band common to the lactones of the santonine group is due to the lactone ring for the reasons given above. Measurements made on camphonolactone, β-butyrolactone and γ-valerolactone showed that the lactonic absorption band in these compounds is outside the range of the instrument. This result does not disagree with the above attribution of the band at 2300 Å to the

lactonic group since it is known that bands shift towards the long waves as the size of the molecule increases. The wavelength of the head of the band depends on the structure of the whole molecule: it is displaced towards the longer waves in santonine owing to the presence of the somewhat unstable conjugated system of double bonds in the molecule. In desmotroposantonine the maximum of this band is outside the range of the instrument owing to the stabilising effect of the aromatic structure which tends to increase the frequencies of the electronic oscillators in the molecule.

Having established a correspondence between the absorption bands and chemical groups in the molecule, the question arises, what may be the reason for the intense absorption of the ketonic band in parasantonide and santonide. According to the classical theory, absorption of light is due to the friction in the motion of the electronic oscillators moving under the influence of the electric field of the light wave. The friction is caused by the transfer of energy from the vibrator to other parts of the molecule (like in the case of coupled pendula: any particular pendulum set into motion loses its energy by setting the others into motion). Or in the language of quantum mechanics, there is a finite probability that the energy of an electron excited by the light wave will go to other parts of the molecule lifting another electron into an

excited state (the case of resonance emission where there is absorption without transfer of energy to other parts of the molecule can be disregarded for organic molecules). According to both theories the vibrators which exchange their energy should be near to one another since the further distant parts of the molecule hardly affect the motion of a particular electron. Applying this condition to the present case, one should expect that in the two lactones with the strong ketonic bands another chromophoric group would be in the vicinity of the ketonic >CO group. This actually happens if it is assumed that the lactone ring is closed to the C-atom 8: the ketonic and the lactonic CO-groups may very well in that case be so close to each other that they mutually disturb their electronic oscillators. There is even the possibility of a co-valency bond (of the nature of a shared electron) between the two CO-groups. As regards the possibility of the enolisation of one of the CO-groups owing to the vicinity of the other, the latter effect is observed in diketones or α - or β-oxocarboxylic acids. It may be noted that it is in such cases (e.g., acetyl acetone and diosphenol, see p.51) that extraordinarily intense absorption bands have been recorded.

B). Optical Activity.

The three highly rotating compounds are remarkable not only for their elevated values of circular dichroism and optical rotation, but also for the fact that there is a Cotton-effect exhibited by fairly strong absorption bands. Such cases have not been recorded in the past since absorption bands of the intensity of $\varepsilon = 10^3$ as a rule do not have an anisotropy factor of the same order of magnitude as the weak bands ($g \sim 10^{-2}$). On the basis of this experimental fact as well as on the ground of theoretical considerations, Kuhn (41) inferred that large anisotropy factors are unlikely to occur in bands where f (the strength of the band) is greater than 10^{-3} (the f-factors are calculated from the formula $f = \frac{mc}{e^2\pi} \frac{1}{N} \int \varepsilon d\nu$. $\int \varepsilon d\nu$ was evaluated by counting the area under the curve).*

An attempt was made to apply Lowry & Hudson's modification of Kuhn's equation for rotatory dispersion (see pp. 9,10) to parasantonide and santonide. The Tables XV and XVI contain the calculated rotations. For parasantonide the circular dichroism curve was approximated to by the equation $\varepsilon_e - \varepsilon_a = 38.e^{-\frac{(\lambda-3000)^2}{244^2}}$ (Tab. XIV). The value 38 for the maximum of the curve is slightly higher than the observed value (36.5) but the higher value was taken in order to obtain a better fitting of the calculated curve to the observed one. The calculated curve for the circular

*f = 1×10^{-2} for the active band of parasantonide,
f = 2.2×10^{-2} " " " " " parasantonide-imide.

Table XIV.

One Term Approximation to the Circular Dichroism Curve of Santonide.

$\varepsilon_l - \varepsilon_r = 31 \times e^{-\left(\frac{\lambda - 3000}{190}\right)^2}$

λ (Å)	$\varepsilon_l - \varepsilon_r$	λ (Å)	$\varepsilon_l - \varepsilon_r$
3000	31	2950	29.4
3100	24.4	2900	24.4
3200	11.9	2850	18.1
3150	18.1	2800	11.9
3050	29.4	2750	5.5
3250	5.5	2700	1.7
3300	1.7		

One Term Approximation to the Circular Dichroism Curve of Parasantonide.

$\varepsilon_l - \varepsilon_r = 38 \times e^{-\left(\frac{\lambda - 3000}{244}\right)^2}$

λ (Å)	$\varepsilon_l - \varepsilon_r$	λ (Å)	$\varepsilon_l - \varepsilon_r$
3000	38	2950	36.5
3050	36.5	2900	32.3
3100	32.3	2850	26.0
3150	26.0	2800	19.4
3200	19.4	2750	13.3
3250	13.3	2700	8.4
3000	8.4	2600	2.9
3400	2.9		

TABLE XV.

Two Term Approximation to the Circular Dichroism of Santonide.

Curve A.

$\varepsilon_e - \varepsilon_l = 27 \times e^{-\left(\frac{\lambda - 2940}{140}\right)^2} + 15 \times e^{-\left(\frac{\lambda - 3120}{100}\right)^2}$

$(\varepsilon_e - \varepsilon_l)_{max} = 27$ $\lambda_0 = 2940$ Å $\theta = 140$ Å

λ (Å)	$\varepsilon_e - \varepsilon_l$	λ (Å)	$\varepsilon_e - \varepsilon_l$
3190	1.10	2890	23.79
3140	3.58	2840	16.98
3090	8.75	2790	8.75
3040	16.98	2740	3.58
2940	23.79	2690	1.10

Curve B.

$(\varepsilon_e - \varepsilon_l)_{max} = 15$ $\lambda_0 = 3120$ Å $\theta = 100$ Å

λ (Å)	$\varepsilon_e - \varepsilon_l$	λ (Å)	$\varepsilon_e - \varepsilon_l$
3270	1.69	3070	12.46
3220	5.89	3020	5.89
3170	12.46	2970	1.69

Fig. XVa. Parasantonide:

— observed circular dichroism

-·-·- one term approximation

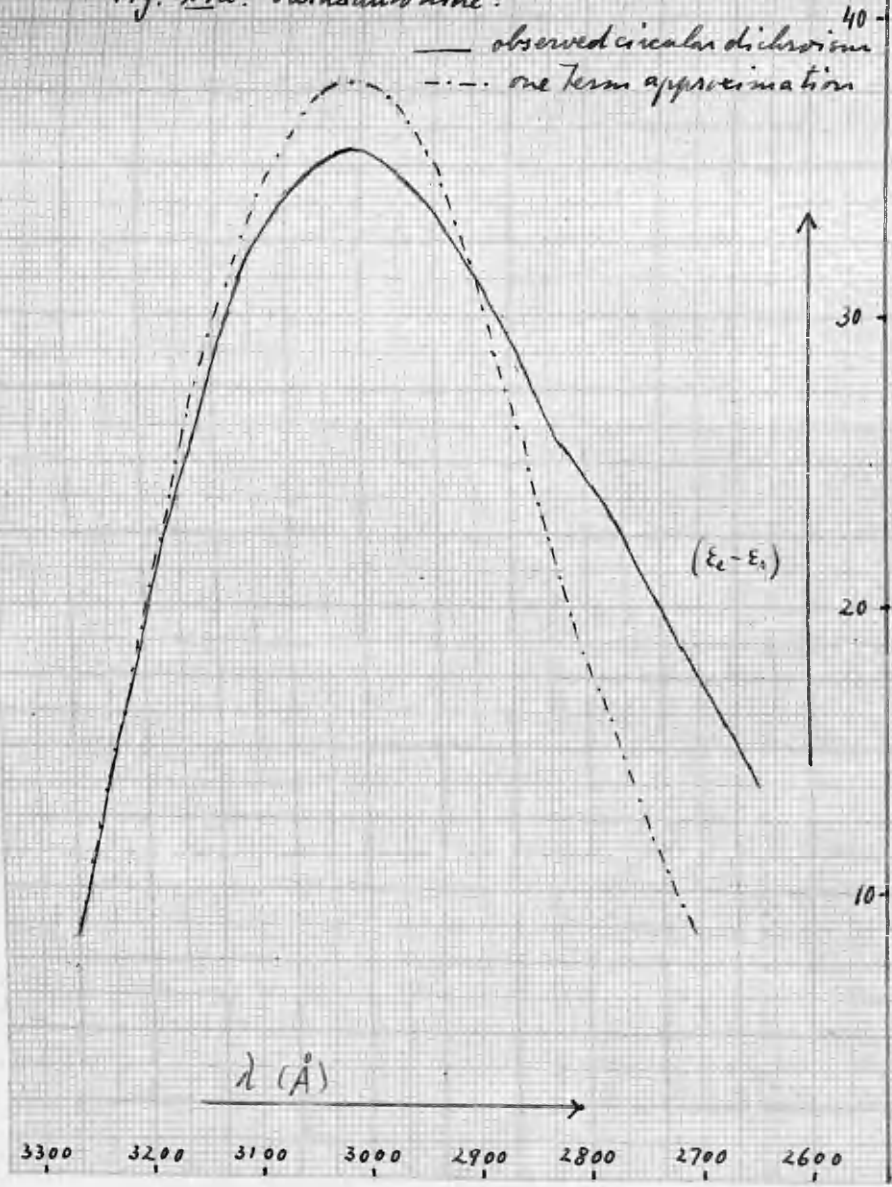


Fig. XVb Santonide — observed circular dichroism

···· subsidiary curves A, B

-·-·- one term approximation

---- A+B (two term approximation)

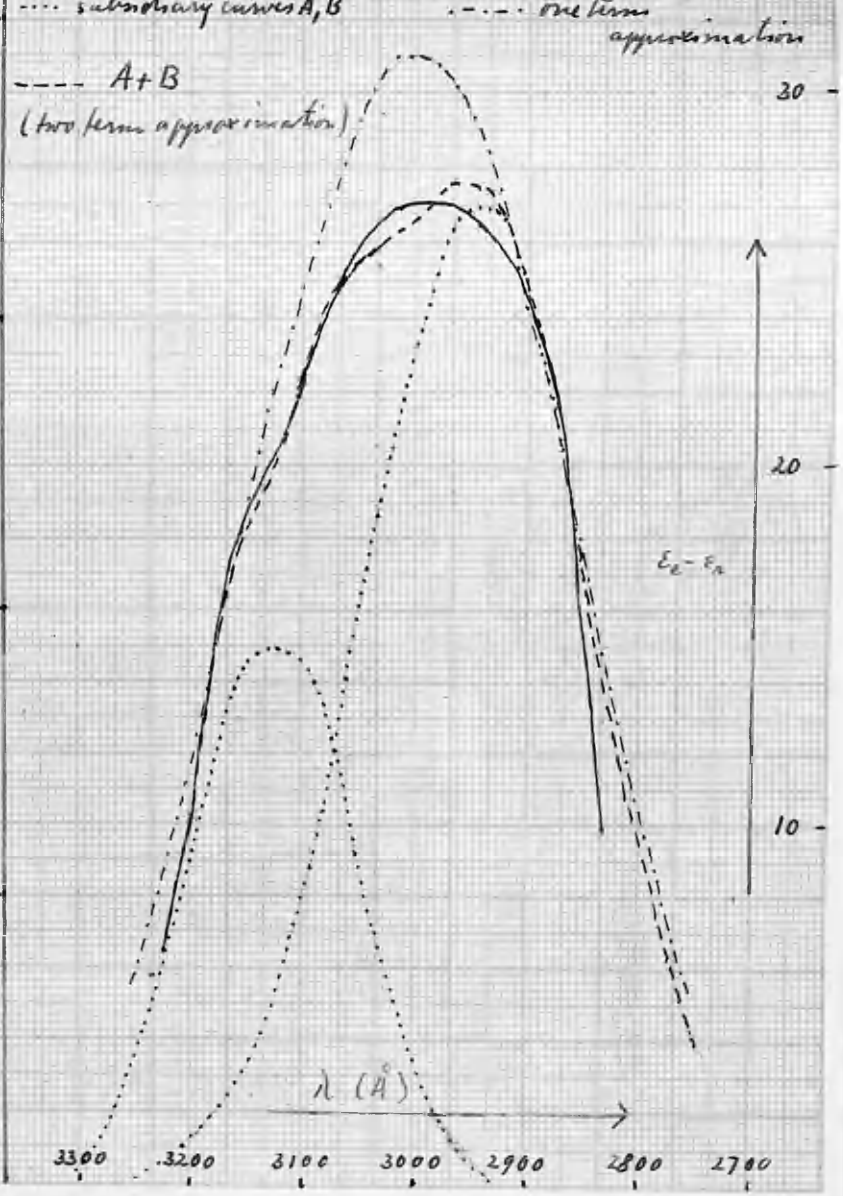


TABLE XVI.

One Term Approximation to the Rotatory Dispersion of Parasantonide.

$\theta = 244\,\text{Å}$ $(\varepsilon_e - \varepsilon_\lambda)_{max} = 38$, $\lambda_0 = 3000\,\text{Å}$ $c = \frac{\lambda - \lambda_0}{\theta}$

λ(Å)	ε	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	$e^{-c^2}\int_0^c e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}$	$[\alpha]$
3781	3.2	0.1564	0.0180	0.1744	6321°
3684	2.8	0.1936	0.0183	0.2119	9651
3586	2.4	0.2353	0.0185	0.2538	12210
3488	2.0	0.3014	0.0188	0.3202	15470
3391	1.6	0.4000	0.0191	0.4191	21320
3342	1.4	0.4565	0.0193	0.4756	24490
3293	1.2	0.5073	0.0194	0.5266	27550
3244	1.0	0.5381	0.0195	0.5575	29610
3220	0.9	0.5407	0.0195	0.5602	29820
3195	0.8	0.5321	0.0196	0.5517	29790
3146	0.6	0.4748	0.0197	0.4945	27110
3073	0.3	0.2762	0.0201	0.2963	16630
3000	0.0	0.000	0.0203	0.0203	1168
2928	-0.3	-0.2762	0.0206	-0.2556	-15050
2855	-0.6	-0.4748	0.0209	-0.4539	-27440
2806	-0.8	-0.5321	0.0211	-0.5110	-31420
2757	-1.0	-0.5381	0.0213	-0.5168	-32230
2660	-1.4	-0.4565	0.0216	-0.4349	-28200
2542	-1.8	-0.3468	0.0220	-0.3248	-21870

TABLE XVII.

One Term Approximation to the Rotatory Dispersion of Santonide.

$\frac{\lambda-\lambda_0}{\theta} = c$, $\theta = 190$, $(\varepsilon_e-\varepsilon_n)_{max} = 31$, $\lambda_0 = 3000$ Å

λ (Å)	c	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	$e^{-c^2}\int_0^c e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}$	$[\alpha]$
3950	5	0.1000	0.0122	0.1122	3563°
3601	3.162	0.1667	0.0144	0.1811	6070
3532	2.8	0.1936	0.0145	0.2081	8292
3494	2.6	0.2122	0.0146	0.2268	9135
3418	2.2	0.2629	0.0148	0.2777	11440
3342	1.8	0.3468	0.0150	0.3618	15240
3266	1.4	0.4565	0.0152	0.4717	20320
3228	1.2	0.5073	0.0153	0.5226	22790
3190	1.0	0.5381	0.0154	0.5535	24420
3171	0.9	0.5407	0.0154	0.5561	24680
3102	0.6	0.4748	0.0155	0.4903	22230
3076	0.4	0.3594	0.0156	0.3750	17160
3038	0.2	0.1947	0.0157	0.2105	9953
3019	0.1	0.0990	0.0158	0.1048	6150
3000	0.0	0.0000	0.0158	0.0158	741
2981	-0.1	-0.0990	0.0159	-0.0831	-3923
2962	-0.2	-0.1947	0.0159	-0.1788	-8494
2924	-0.4	-0.3594	0.0160	-0.3434	-16530
2886	-0.6	-0.4748	0.0161	-0.4587	-22380
2848	-0.8	-0.5321	0.0162	-0.5159	-25500
2810	-1.0	-0.5381	0.0163	-0.5218	-26160
2772	-1.2	-0.5073	0.0164	-0.4909	-24890
2734	-1.4	-0.4565	0.0166	-0.4399	-22650
2696	-1.6	-0.4000	0.0167	-0.4167	-21730
2658	-1.8	-0.3468	0.0167	-0.3301	-17490

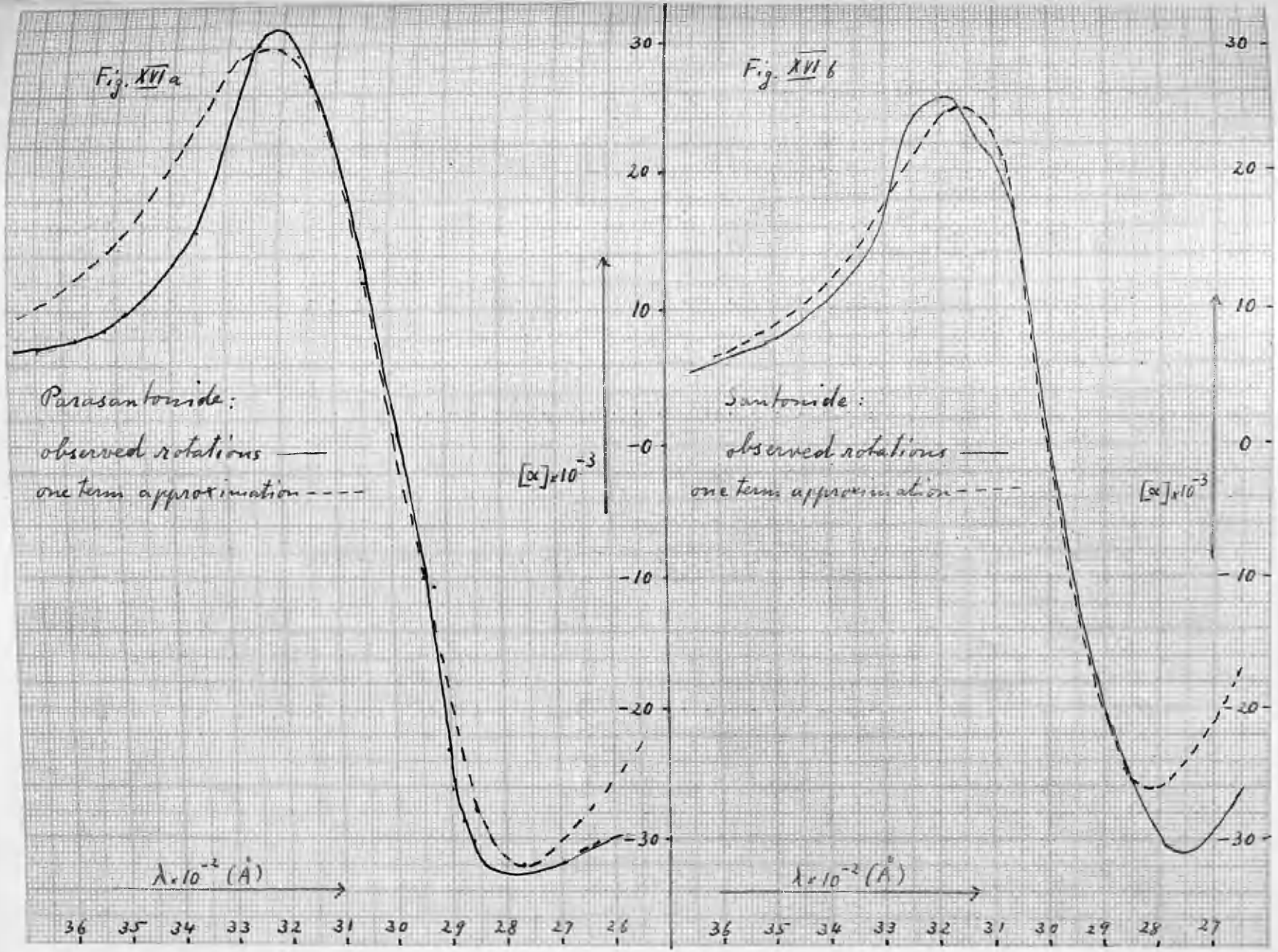


Fig. XVI a
Parasantonide:
observed rotations ——
one term approximation - - -
[α]×10⁻³
λ×10⁻² (Å)
36 35 34 33 32 31 30 29 28 27 26
30 20 10 -0 -10 -20 -30
Fig. XVI b
Santonide:
observed rotations ——
one term approximation - - -
[α]×10⁻³
λ×10⁻² (Å)
36 35 34 33 32 31 30 29 28 27
30 20 10 0 -10 -20 -30

dichroism is shown in Fig. XVa. The rotatory dispersion was calculated with the constants $(\varepsilon_\ell - \varepsilon_r)_{max} = 38$ $\theta = 244$ Å, $\lambda_o = 3000$ Å (Fig. XVb). The agreement is not very satisfactory. The greatest discrepancy between the calculated and the observed rotations is on the long wave-length approach to the positive maximum where the observed curve is very steep.

For santonide the agreement between observed and calculated values (see Table XIVb, Fig. XVIb) is slightly better: the values given in Table XVII have been calculated with the parameters $(\varepsilon_\ell - \varepsilon_r)_{max} = 31$, $\theta = 190$ Å, $\lambda_o = 3000$ Å. (FXVIb) Here $(\varepsilon_\ell - \varepsilon_r)_{max}$ had to be chosen considerably higher than the experimental value of 27 in order to get even a tolerably satisfactory agreement between the curve calculated by means of the approximation formula and the observed circular dichroism curve owing to the narrowness and steepness of the latter. The main deficiency of the calculated curve again lies in the region to the left of the positive maximum and the same reasoning as in the case of parasantonide also applies here.

A better approximation both to the observed circular dichroism and rotatory dispersion curves could be obtained when the circular dichroism band was considered as composite. The best results for both curves were reached by assuming the presence of two subsidiary bands (curve A with the maximum $(\varepsilon_\ell - \varepsilon_r) = 27$, $\theta = 140$, $\lambda_o = 2940$ Å, and curve B

TABLE XVIII.

Two Term Approximation to the Rotatory Dispersion of Santonide.

Curve A. $\theta = 140$ Å $\quad \varepsilon_\ell - \varepsilon_{r_{max}} = 27, \quad \lambda_o\ 2940, \quad c = \frac{\lambda - \lambda_o}{\theta}$

λ (Å)	c	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_o)}$	$e^{-c^2}\int_0^c e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_o)}$	$[\alpha]$
3800	5.8	0.0863	0.0104	0.0967	3057
3660	4.8	0.1040	0.0106	0.1146	3840
3510	3.8	0.1330	0.0109	0.1439	4923
3360	2.8	0.1936	0.0111	0.2047	7314
3300	2.4	0.2353	0.0112	0.2465	9436
3240	2.0	0.3014	0.0113	0.3127	11590
3180	1.6	0.4000	0.0114	0.4114	15630
3120	1.2	0.5073	0.0115	0.5189	19970
3075	0.9	0.5407	0.0116	0.5523	21580
3030	0.6	0.4748	0.0117	0.4863	19300
2985	0.3	0.2762	0.0118	0.2880	11570
2895	-0.3	-0.2762	0.0120	-0.2642	-10950
2850	-0.6	-0.4748	0.0121	-0.4627	-19460
2805	-0.9	-0.5407	0.0122	-0.5285	-22630
2760	-1.2	-0.5073	0.0123	-0.4950	-21550
2700	-1.6	-0.4000	0.0124	-0.3876	-17240
2640	-2.0	-0.3014	0.0125	-0.2889	-13130
2580	-2.4	-0.2353	0.0127	-0.2126	-9902

TABLE XVIII (Contd.)

Two Term Approximation to the Rotatory Dispersion of Santonide.

Curve B. $\theta = 100$ $(\xi_e - \xi_1)_{max} = 15.$ $\lambda_0 = 3120\,\text{Å}$ $c = \frac{\lambda - \lambda_0}{\theta}$

λ (Å)	c	$e^{-c^2}\int_0^c e^{x^2}dx$	$\frac{\theta}{2(\lambda+\lambda_0)}$	$e^{-c^2}\int_0^c e^{x^2}dx + \frac{\theta}{2(\lambda+\lambda_0)}$	$[\alpha]$
3800	6.8	0.0735	0.0072	0.0807	948
3700	5.8	0.0862	0.0073	0.0935	1129
3600	4.8	0.1004	0.0074	0.1078	2073
3500	3.8	0.1316	0.0075	0.1391	2815
3400	2.8	0.1936	0.0077	0.2013	4193
3320	2.0	0.3014	0.0078	0.3092	6598
3280	1.6	0.4000	0.0078	0.4078	8808
3240	1.2	0.5073	0.0079	0.5152	11121
3210	0.9	0.5407	0.0079	0.5486	12110
3180	0.6	0.4748	0.0080	0.4828	10750
3150	0.3	0.2762	0.0080	0.2842	6390
3090	-0.3	-0.2762	0.0081	-0.2681	-6145
3060	-0.6	-0.4748	0.0081	-0.4667	-10690
3030	-0.9	-0.5407	0.0082	-0.5325	-12320
3000	-1.2	-0.5073	0.0082	-0.4991	-11790
2960	-1.6	-0.4000	0.0082	-0.3918	-9374
2920	-2.0	-0.3014	0.0083	-0.2931	-7065
2840	-2.8	-0.1936	0.0084	-0.1852	-4619
2720	-4.0	-0.1250	0.0086	-0.1267	-3292
2620	-5.0	-0.1000	0.0087	-0.0913	-2460

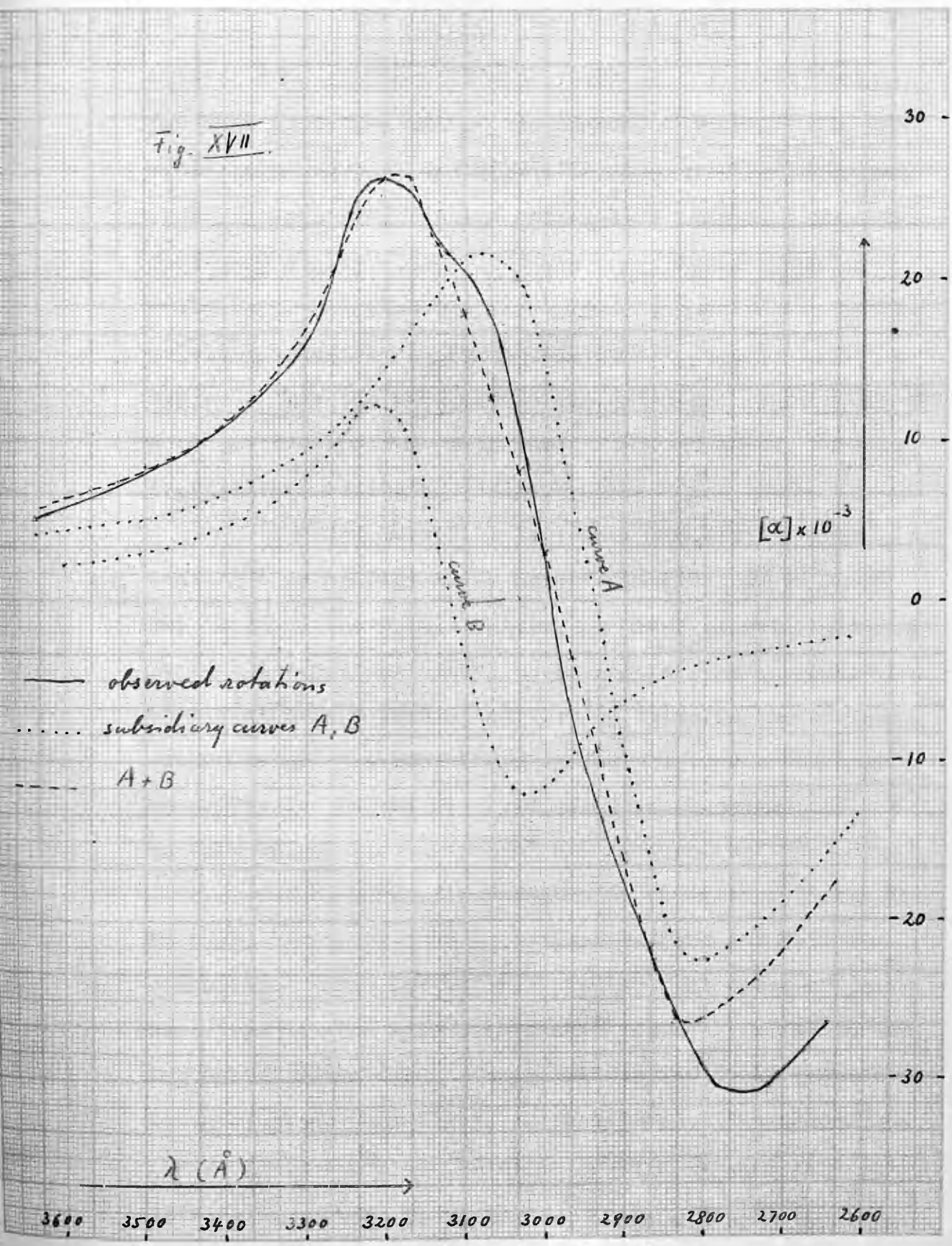


Fig. XVII. Santonide: Two Term Approximation to the Rotations

with $(\varepsilon_\ell - \varepsilon_r)_{max} = 15$, $\theta = 100$ Å, $\lambda_o = 3120$ Å. A justification for this procedure can be seen from the fact that both the extinction and the circular dichroism curve of santonide show a slight bulge in the region near 3160 Å. Even the fact that a single term of Gauss's error distribution curve, which represents a fairly good approximation in the majority of cases, is inadequate in the present case, suggests that the band may be composite. Figs. XVb and XVII show the results thus obtained. The agreement, however, is still not perfect. (Tables XV, XVIII)

It would therefore seem that the Cotton-effect in santonide is brought about by superposition of at least two bands. There is, however, no proof of this being so: it is quite possible that the failure of the approximation by a single term error-distribution curve to the circular dichroism and the corresponding failure of the one term approximation to the observed rotatory dispersion is due to theoretical limitations of the mathematical analysis.

In the case of parasantonide preliminary attempts to carry out a two-term approximation were not very encouraging: there are indications that the curve of parasantonide is even more complicated than that of santonide. The calculations being rather tedious and their results not being of great importance, these attempts were abandoned.

Discussing the question whether the observed Cotton-effects are simple or composite, it should be noted that in

all three cases the maxima of absorption, circular dichroism curves and the reversal of sign of the rotatory dispersion curve occur at practically the same wave length (in the case of parasantonide-imide there is a slight difference). This fact does not support the assumption of a composite nature of the Cotton-effects since it is not very likely that two Cotton-effects would be superimposed in such a way that the characteristics of simple Cotton-effect are exhibited by the resulting curve. The question must therefore remain entirely open.

Kuhn's equation was not applied to the rotatory dispersion of parasantonide-imide since in this case the observations were not accurate enough to draw any conclusions from a possible agreement or disagreement with the calculated values.

From the observed anisotropy factor Kuhn drew conclusions about the dimensions of the model of coupled vibrators: he deduced the formula $d \gtrsim g\frac{\lambda}{4\pi}$ (loc.cit.) where g is the mean anisotropy factor within the band and d the distance between the two coupled vibrators. For parasantonide ($\lambda = 3\times10^{-5}$cm., $\bar{g} \cong 3\times10^{-2}$) the formula gives $d \gtrsim 16$ Å, which is certainly impossible as the diameter of the whole molecule must be considerably less than that. Kuhn himself found many cases where d was greater than the atomic dimensions.

Since, however, in all these cases where d was found to be of greater order of magnitude than the molecular diameter, the absorption was weak ($f \leq 10^{-3}$). Kuhn & Bein (41) modified the formula for d, taking into account contributions by quadrupole as well as dipole oscillators. (It is interesting to note that Condon, Altar and Eyring (20) state that quadrupole vibrations do not contribute towards circular dichroism). Quadrupole moments can account only for very weak absorption ($f \sim 10^{-6}$) and since the circular dichroism $\varepsilon_l - \varepsilon_r$ certainly cannot exceed the total absorption, it is seen that a quadrupole vibration could not substantially contribute to the circular dichroism in either parasantonide, santonide or parasantonide-imide where f for the $(\varepsilon_l - \varepsilon_r)$-band is of the order 10^{-3} - 10^{-4}. It is therefore necessary to use Kuhn's first formula for the calculation of d. The result $d \geq 16$ Å is even more improbable in the present case because according to Kuhn's theory a strong coupling force is necessary to cause an appreciable anisotropy factor in a strong band. It is quite impossible to assume that an electronic oscillator is influenced by another oscillator from which it is separated by a distance of 16 Å, much less can a strong coupling force be supposed to exist between the two. All these facts show that Kuhn's model is not suited to explain the optical activity of the high-rotating lactones of the santonine group.

Most modern theories are not suitable for the discussion of the optical activity of complicated molecules (see Introduction). Condon, Altar and Eyring's (20) theory makes an exception. It suggests that vicinal action by other substituents causes optical activity in an electronic oscillator. If, therefore, compounds of otherwise similar structure differ in their optical activity, it must be assumed that the structure near the absorbing group which controls the optical activity in the visible region is different. Optical activity of a chromophoric group will increase with the asymmetric disturbance exerted on it by the electric field of the neighbouring substituents. (This result of the theory is the explanation of Kuhn's rather empirical vicinal rule). The previous discussion has shown that there is, in fact, a strong disturbing influence on the electronic structure of the ketonic CO-group caused by the proximity of the lactone group. The rotatory strength R can be calculated (see pp.13,14). It is of the order of unity in contradiction to the result derived by the theory that R 1 in general. It thus appears that neither (a/p/b) nor (b/m/a) can be small compared with unity in the present case, so that the conditions under which a first order approximation in the perturbation theory can be applied do not exist in the present case. $R \cong f \cdot g \cdot \frac{3}{2\pi} \cdot \frac{\lambda}{a} = 1{\cdot}4\times10^{-2} \times 3{\cdot}7\times10^{-2} \times \frac{3}{2\pi} \times \frac{3\times10^{-5}}{0{\cdot}52\times10^{-8}} \sim 1$ for parasantonide. $R = 2{\cdot}2\times10^{-2} \times 2{\cdot}8\times10^{-2} \times \frac{3}{2\pi} \times \frac{3{\cdot}07\times10^{-5}}{0{\cdot}52\times10^{-8}} \cong 1{\cdot}7$ for parasantonide-imide.

In discussing the Cotton-effect of some ketones Lowry, Simpson and Allsopp (42) suggested that it is caused by the motion of one of the two "lone pair" electrons of the O-atom. This assumption was based on an analysis by Mulliken of the absorption spectrum of formaldehyde (43);(43A).The attribution of the optical activity in parasantonide, santonide and parasantonide-imide to the motion of an electron, in a strongly asymmetric field in which it moves, is plausible since both chemical and optical properties (pp.48,51) suggest that neighbouring groups are decisively influencing the structure of the ketonic CO-group. (In the case of the imide the group in which the asymmetric electron moves is of course the C = NH, which has an electronic structure similar to that of the -CO- group: both have 10 electrons in the outer shell).

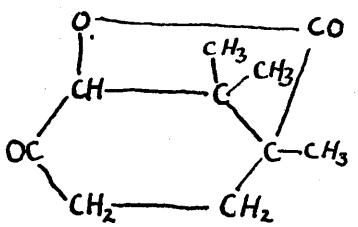
PART II.

Absorption Spectrum, Circular Dichroism and Rotatory Dispersion of Camphonolactone in the Ultra-Violet.

PART II.

Absorption Spectrum, Circular Dichroism and Rotatory Dispersion of Camphonolactone in the Ultra-Violet.

In order to extend the investigation on the optical properties of keto-lactones, the Cotton-effect of camphonolactone was measured. This substance was chosen because it is one of the few comparatively simple compounds of that type where the CO and the lactone ring are close enough to influence one another.



Preparation of the substance.

a). $\alpha\alpha'$ -dibromocamphor was prepared according to Lowry (48) by the action of bromine on camphor at 100°, m.p. 60°. $[\alpha]_D = 60°$.

b). Dibromocampholide was obtained by oxidising $\alpha\alpha'$ -dibromocamphor with fuming nitric acid (Forster (49)), m.p. 152°.

c). Camphonolactone (49) was prepared by hydrolysing dibromocampholide with alcoholic potash, m.p. 194°, $[\alpha]_D = -117.3°$.

Absorption Spectrum (Table I, Fig. I).

The absorption of camphonolactone was measured in alcohol and in water. In alcohol a band is observed with the maximum $\varepsilon = 22.9$ at $\lambda = 2970$ Å. In water $\varepsilon_{max} = 29.5$ at $\lambda = 2880$ Å. There is thus a considerable difference between the extinction curves in the two solvents, water having the effect of shifting the absorption band towards the short waves. This result is in agreement with the investigations made (44) on the solvent action on the ketonic absorption. It was found that water with its large dipole moment strongly polarises the -CO-group unless the latter is protected against the approach of the solvent molecules by neighbouring substituents. Below = 2590 Å in alcohol and $\lambda = 2430$ Å in water the absorption increases steeply towards the ultra-violet end of the region: the highest value was measured for $\lambda = 2184$ Å ($\varepsilon = 221$) where the maximum is not yet reached. According to all probability this absorption is part of the lactonic absorption band which is beyond the range of the instrument. Comparing the extinction curve with the extinction curves of parasantonide and santonide, it is noted that the two bands in the spectrum of camphonolactone are shifted towards the short wave lengths because the molecule is smaller and more saturated.

TABLE I.

A). Absorption Spectrum of Camphonolactone in Water.

Solution a). 0.3460 g. in 100 cm^3.

λ(Å)	Sector reading	ε	λ(Å)	Sector reading	ε
3207	0.1	4.9	2404	0.5	24.6
3160	0.2	9.8	2377	0.6	29.5
3098	0.3	14.7	2366	0.7	34.4
3031	0.4	19.7	2350	0.8	39.3
2968	0.5	24.6	2339	0.9	44.2
2877	0.6	29.5	2323	1.0	49.1
2793	0.5	24.6	2315	1.1	54.1
2724	0.4	19.7	2308	1.2	59.0
2563	0.3	19.7	2299	1.3	63.9
2448	0.3	14.7	2297	1.4	68.8
2425	0.4	19.7	2293	1.5	73.7

Solution b). 0.0692 g. in 100 cm^3.

2343	0.1	24.6	2252	0.6	147.4
2303	0.3	73.7	2230	0.7	172.0
2291	0.4	98.3	2206	0.8	196.5
2277	0.5	122.8	2184	0.9	221.0

B). Absorption Spectrum of Camphonolactone in Alcohol.

0.9670 in 100 cm^3.

3359	0.1	1.9	2887	1.1	21.0
3293	0.2	3.8	2847	1.0	19.2
3236	0.3	5.7	2808	0.9	17.1
3211	0.4	7.6	2776	0.8	15.2
3193	0.5	9.5	2747	0.7	13.3
3168	0.6	11.4	2698	0.6	11.4
3156	0.7	13.3	2655	0.5	9.5
3121	0.8	15.2	2616	0.4	7.6
3096	0.9	17.1	2566	0.3	5.7
3070	1.0	19.2	2516	0.3	5.7
3031	1.1	21.0	2471	0.4	7.6
2985	1.2	22.8	2410	0.8	15.2
2968	1.2	22.8	2405	1.2	22.8

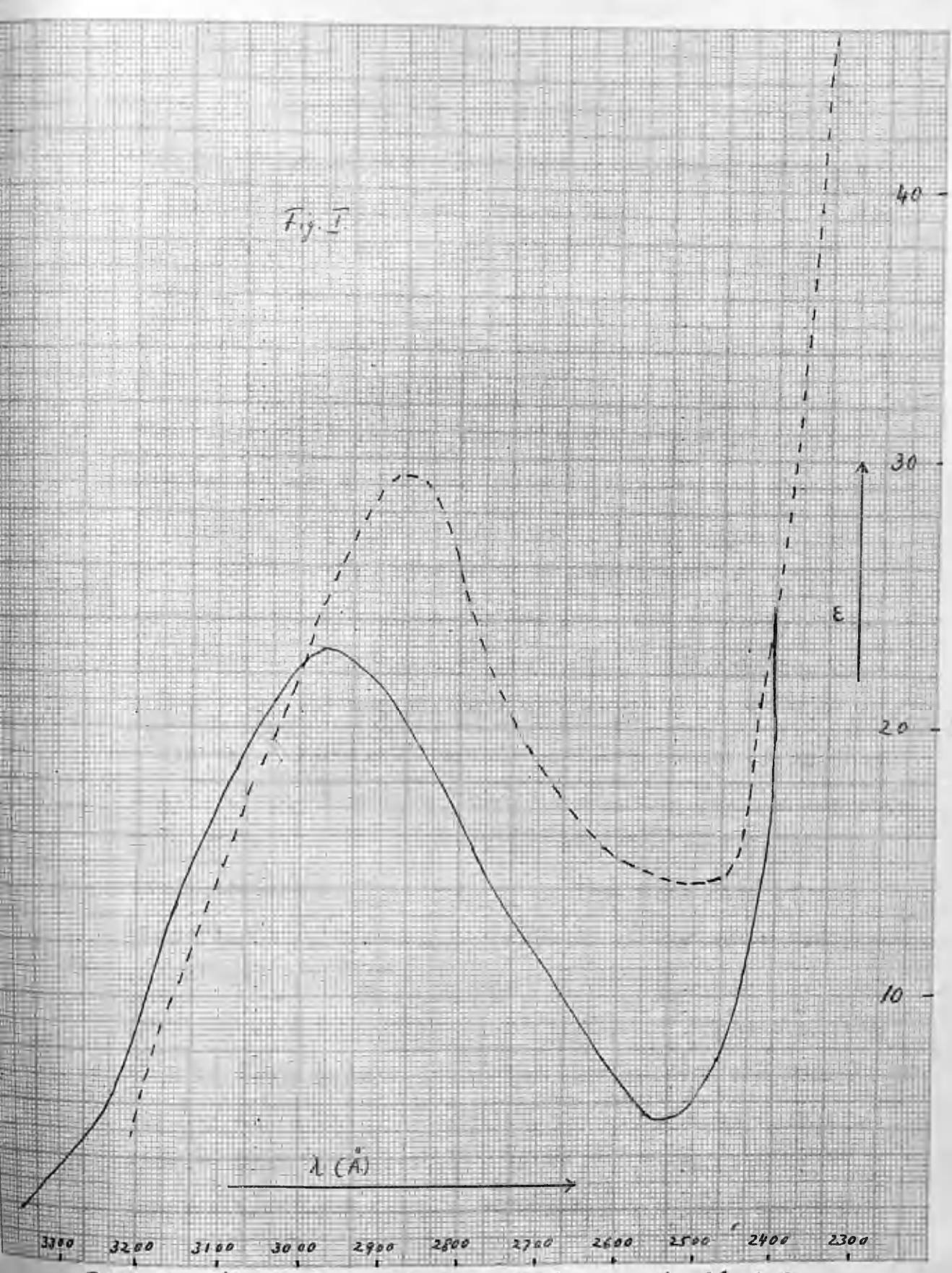


Fig. I. Absorption Spectrum of Camphonolactone —— in Alcohol
--- in Water.

Rotatory Dispersion (Table II, Fig. II).

Camphonolactone exhibits a Cotton-effect in the region of its ketonic absorption band. There is a negative maximum of the rotations at λ = 3230 Å of $[\alpha]$ = −1550°. The reversal of sign occurs at λ = 3030 Å and does not coincide with the maximum of the absorption band in either water or alcohol (it is λ = 2970 Å in alcohol). It is seen from the graph that a positive maximum of the dispersion curve is not reached although it is clearly indicated by the shape of the curve. The slope of the curve between λ = 2860 Å and λ = 2580 Å is much smaller than in the neighbouring regions: this fact must be attributed to the fall of the rotation contributed by the ketonic band to the right of the positive maximum. The fact that the positive rotations in that region are much smaller than the negative maximum suggests that there must be a subsidiary negative contribution to the rotations in that region. The sharp rise of the dispersion curve below λ = 2600 Å, on the other hand, proves the presence of a positive contribution - probably from the optically active lactone band. This change of sign of the subsidiary rotation between 2750 and 2600 Å may be due either to a Cotton-effect exhibited by a subsidiary band in that region or to the superposition of the positive contribution of the lactonic band and the

TABLE II.

Rotatory Dispersion of Camphonolactone in Alcohol.

1. Visible Spectrum.

c = 1.7424 g. in 100 cm^3. l = 10 cm.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
6800	-1.64°	-93.9°	5100	-2.80°	-157.1°
6350	-1.84	-100.6	4900	-3.07	-172.8
5895	-2.00	-114.8	4750	-3.63	-208.4
5460	-2.31	-132.6	4600	-3.78	-217.0
5250	-2.59	-148.7			

2. Ultra-violet Region.

Solution a). c = 1.7424 g. in 100 cm^3. l = 10 cm.

λ (Å)	α	$[\alpha]$	λ (Å)	α	$[\alpha]$
4039	-5.2°	-298.5°	3420	-8.2°	-941.3°
3796	-7.2	-413.2	3410	-15.2	-872.7
3748	-8.2	-470.7	3405	-16.2	-929.8
3678	-9.2	-528.0	3394	-9.2	-1056
3610	-10.2	-585.5	3391	-9.7	-1114
3548	-11.2	-642.8	3380	-10.2	-1170
3520	-12.2	-700.3	3377	-10.7	-1228
3477	-13.2	-757.7	3350	-11.2	-1285
3440	-14.2	-815.1			

Solution b). c = 1.3070 g. in 100 cm^3.

4205	-0.40°	-306°	3143	-1.90°	-1454°
4039	-0.50	-383	3098	-1.80	-1378
3804	-0.60	-419	3090	-1.40	-1071
3654	-0.70	-535	3069	-0.50	-383
3512	-0.80	-613	2968	0.50	383
3420	-0.80	-613	2857	1.00	765
3373	-1.00	-765	2579	1.40	1071
3343	-1.40	-1071	2536	1.80	1378
3312	-1.80	-1378	2519	2.10	1607
3292	-1.90	-1454	2485	2.20	1683
3267	-2.00	-1530	2475	2.30	1760
3187	-2.00	-1530	2461	2.40	1837.

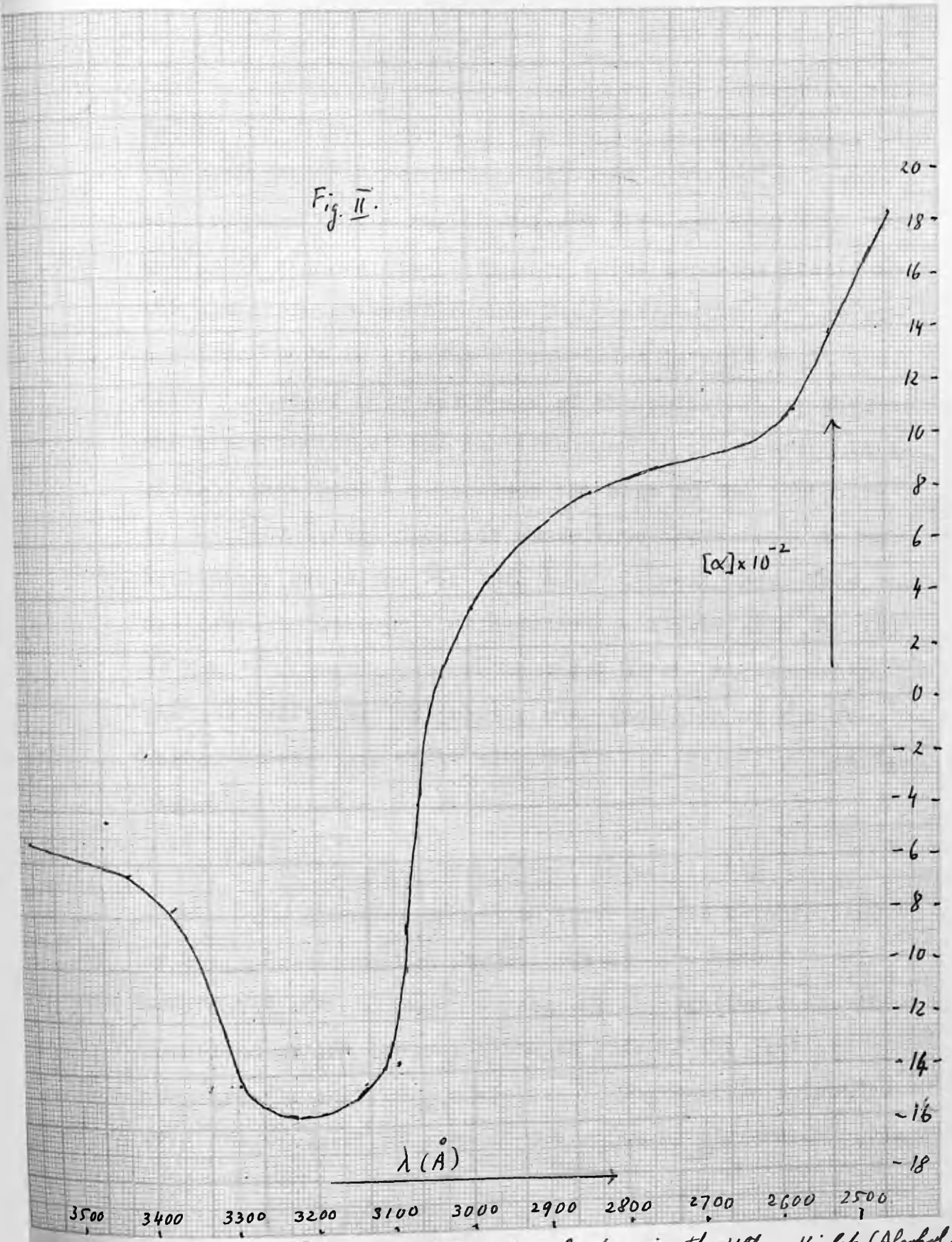


Fig. II. Rotatory Dispersion of Camphonolactone in the Ultra-Violet. (Alcohol)

negative subsidiary rotation caused by the absorption bands in the far ultra-violet. The latter is more likely, as the absorption spectrum does not show any sign of a subsidiary band in the region between 2750 and 2600 Å. The change of sign of the subsidiary curve explains itself by the plausible assumption that the contribution of the absorption bands in the far ultra-violet is only small and almost constant over the range of the polarimeter, whereas the contribution of the lactonic band in the nearer ultra-violet $\lambda \sim$ 2000 Å determines the sign in the region up to $\lambda \sim$ 2600 Å, but does not contribute appreciably to the subsidiary curve for $\lambda >$ 2900 Å. It would have been desirable to attempt a mathematical analysis with the aid of Kuhn's formula, but the accuracy of the measurements was not sufficient to justify the resolution of the observed curves into their components. (See also circular dichroism below).

Circular Dichroism (Table III, Fig. III).

The circular dichroism curve of the ketonic band of camphonolactone has its maximum at λ = 3030 Å. In accordance with Natanson's rule, it is negative since the rotations at the long wave length side of the band are negative. $(\varepsilon_\ell - \varepsilon_r)_{max} = -1.17$. The maximum coincides with the reversal of sign of the rotatory dispersion curve

TABLE III.

Circular Dichroism and Anisotropy Factor of Camphonolactone in Alcohol.

0.1307 g. in 10 cm^3 alcohol. l = 1 cm.

λ(Å)	$-\alpha$	$-(\varepsilon_\ell - \varepsilon_r)$	ε	$-\frac{\varepsilon_\ell - \varepsilon_r}{\varepsilon}$
3312	0.55°	0.234	2.85	0.082
3275	0.95	0.402	5.25	0.076
3209	1.35	0.571	7.4	0.077
3160	1.75	0.741	12.0	0.062
3132	2.25	0.952	14.8	0.064
3120	2.35	0.995	15.7	0.063
3116	2.45	1.066	15.9	0.067
3097	2.55	1.079	17.0	0.064
3087	2.65	1.121	17.7	0.063
2954	2.65	1.121	22.7	0.049
2931	2.55	1.079	22.1	0.049
2928	2.45	1.066	22.05	0.048
2927	2.35	0.995	22.0	0.045
2922	2.25	0.952	21.9	0.043
2885	2.20	0.927	20.9	0.044
2824	1.70	0.717	18.4	0.039
2766	1.50	0.633	14.7	0.043
2715	1.10	0.464	12.0	0.039
2670	0.70	0.288	10.0	0.029
2590	0.40	0.169	6.7	0.025

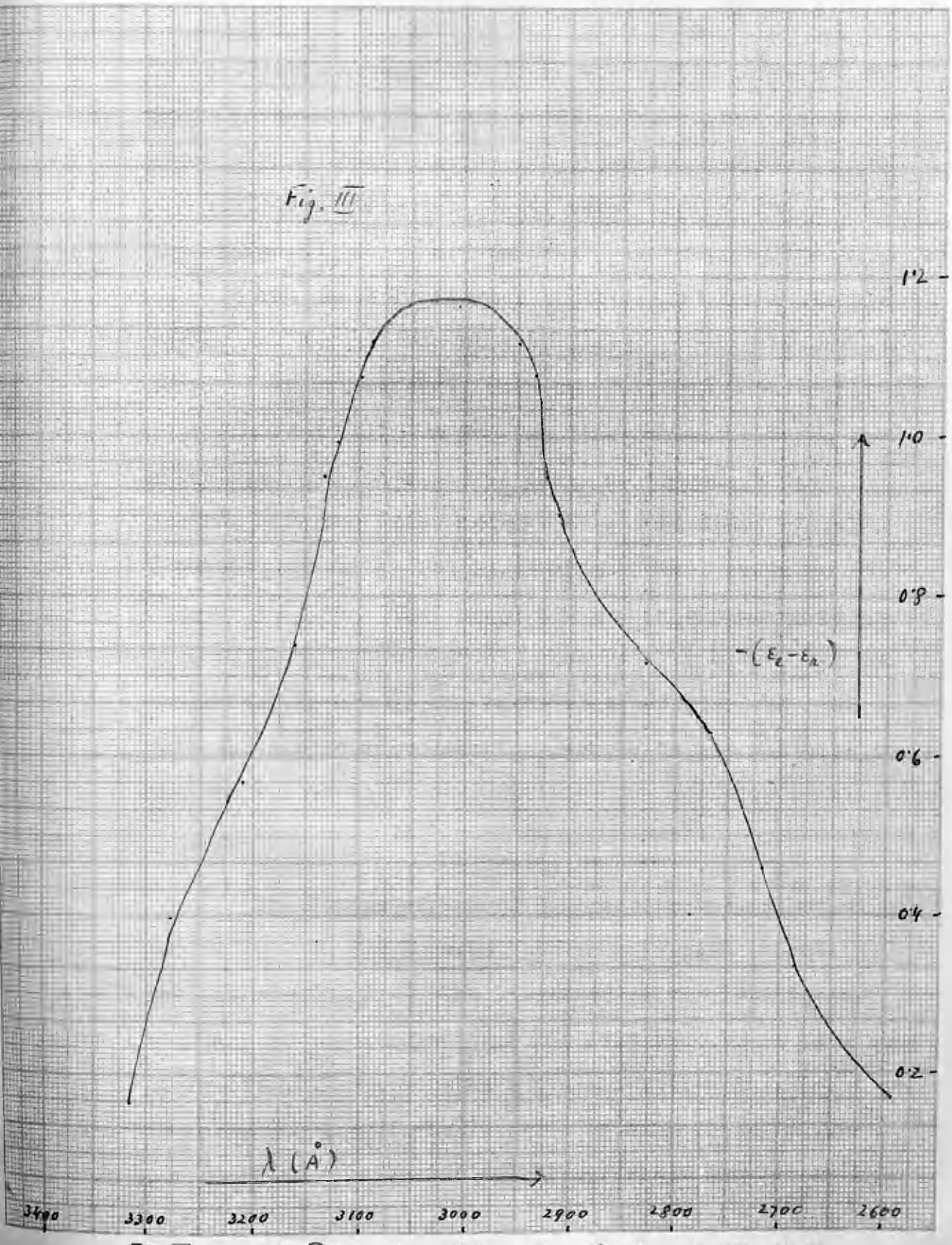


Fig. III. Circular Dichroism of Camphoroxalactone in Alcohol.

but not with the maximum of the absorption curve. This is in agreement with Lowry's (50) observation that in ketonic bands the rotation and circular dichroism curves are shifted towards the longer wave lengths compared with the absorption curve of the band.

The curve is steeper on the side of the visible region and can in this part be approximatedto by Gauss's error distribution curve with the following constants: $\lambda_0 = 3030$ Å, $(\varepsilon_e - \varepsilon_i)_{max} = 1.17$, $\Theta = 230$ Å. The disagreement between the calculated and the measured curve on the short wave lengths side may arise because of a subsidiary circular dichroism curve. The shape of the curve seems to suggest this. The irregularities in the measurements (the bulge at λ = 2760 Å), however, lie within the experimental errors of the instrument and the mere fact that the simple approximation formula is not suitable for the whole band does not entitle to any definite conclusions.

Discussion.

The Cotton-effect of camphonolactone is not simple but it is - as far as magnitude is concerned - certainly not extraordinary. The intensity of the ketonic absorption is quite normal and the fact that there is a considerable difference between the absorption in alcohol and in water shows that the $\backslash C O$ group is unprotected against the polarising influence of the solvent molecules as it

would be if other substituents were near to it. This fact as well as the chemical formula (from which it appears that the ketonic and the lactonic >CO groups are not near to one another) show that none of the causes which were suggested to account for the abnormal optical activity in the santonine derivatives are present in this case.
The sharp increase of the rotation towards the short waves suggests a Cotton-effect of opposite sign to that of the ketone band in the lactone band. The anisotropy factor (see Table III) is not constant but decreases towards the short wave-lengths. This again is in agreement with Lowry's rule for the optical activity of ketonic bands (see p.66). An additional reason for the sharp fall of the absolute value of the anisotropy factor towards the short waves may be the superposition of a positive contribution from the lactonic band to the negative anisotropy factor of the first band.

Absorption Spectra of β-Butyrolactone and γ-Valerolactone in the Ultra-Violet.

As no extinction curves of simple lactones seem to have been recorded in the literature, it was necessary to carry out some measurements on such compounds in order to see whether these are compatible with the attribution of the short wave-length absorption bands in the santonine group to the lactone ring.

Preparation of the Substances.

1). β -Butyrolactone.

a). β -bromobutyric acid was prepared by the action of HBr on crotonic acid (45). The acid was distilled in vacuo (13 mm.).

b). β -butyrolactone (46). β-bromobutyric acid was neutralised with Na_2CO_3 solution and heated to 40-45° for several hours during which period the solution was repeatedly extracted with ether. After drying the extract with $CaCl_2$ and removing the ether, the lactone was repeatedly distilled in vacuo (72-73°, 29 mm.) in order to obtain an optically pure sample.

2). γ -Valerolactone.

The lactone was prepared by reducing laevulinic acid with Na in alcohol(47) and subsequent acidification. The lactone was extracted with ether and repeatedly rectified in vacuo.

Measurements (Tables A, B). (Fig. A).

It is seen from the graphs that no absorption bands were observed in both lactones, but merely an increase of the absorption towards the ultra-violet end of the spectrum. Bearing in mind that even the much heavier molecule of camphonolactone and even that of l-desmotroposantonine showed no maximum of the lactonic absorption in the region accessible to measurements, this result is what should be expected.

TABLE A.

Absorption of γ-Valerolactone in Hexane.

0.0856 g. in 10 cm^3.

λ (Å)	Section reading	ε	λ (Å)	Section reading	ε
2507	0.1	1.17	2365	0.9	10.5
2483	0.2	2.34	2362	1.0	11.7
2460	0.3	3.51	2351	1.1	12.9
2450	0.4	4.67	2330	1.2	14.0
2434	0.5	5.84	2318	1.3	15.2
2423	0.6	7.01	2296	1.4	16.4
2404	0.7	8.18	2284	1.5	17.5
2387	0.8	9.37			

TABLE B.

Absorption of β-Butyrolactone in Alcohol.

0.0881 g. in 10 cm^3.

λ (Å)	Section reading	ε	λ (Å)	Section reading	ε
2435	0.3	2.9	2321	1.0	9.76
2376	0.4	3.90	2315	1.1	10.74
2355	0.5	4.89	2308	1.2	11.71
2340	0.6	5.86	2302	1.3	12.69
2328	0.7	6.83	2300	1.4	13.66
2331	0.8	7.81	2281	1.5	14.64
2326	0.9	8.77			

Fig. A

Absorption of γ-Valerolactone

in Hexane

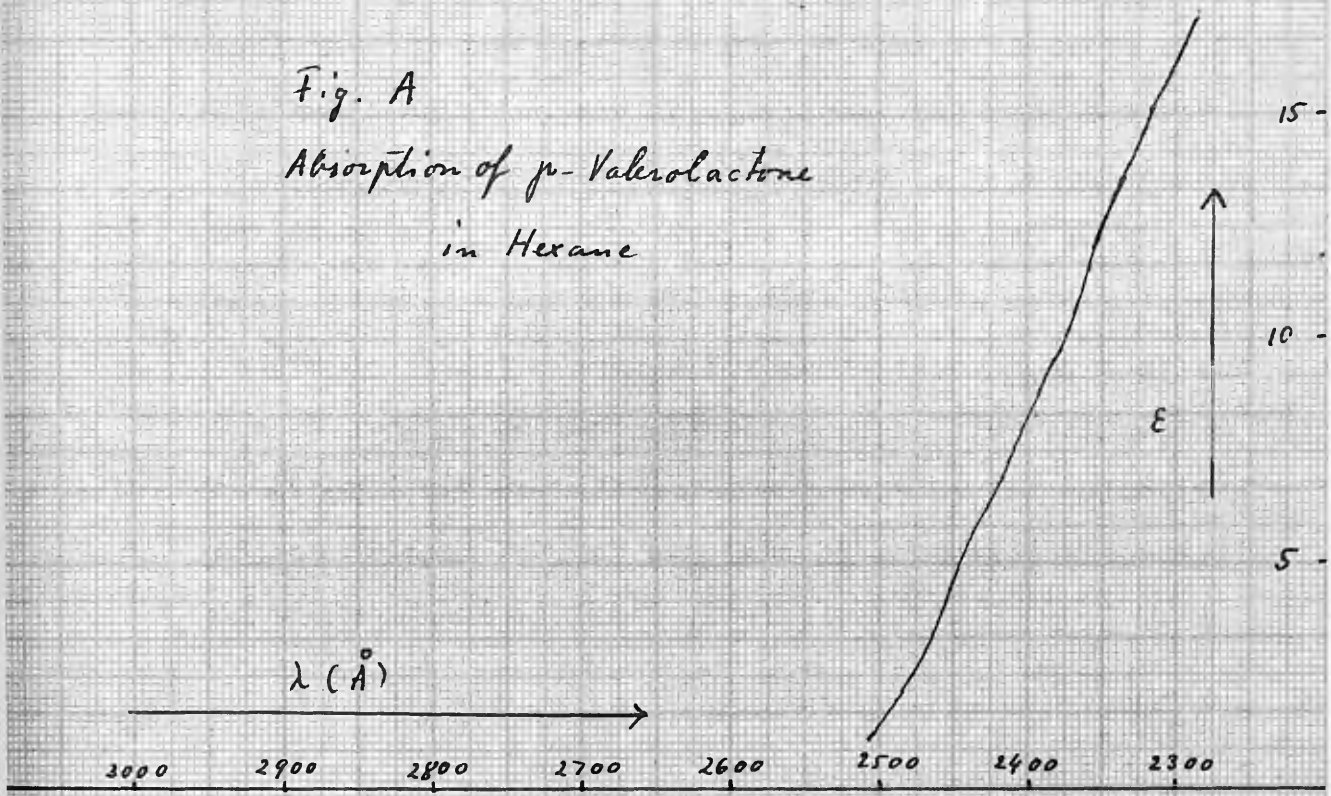
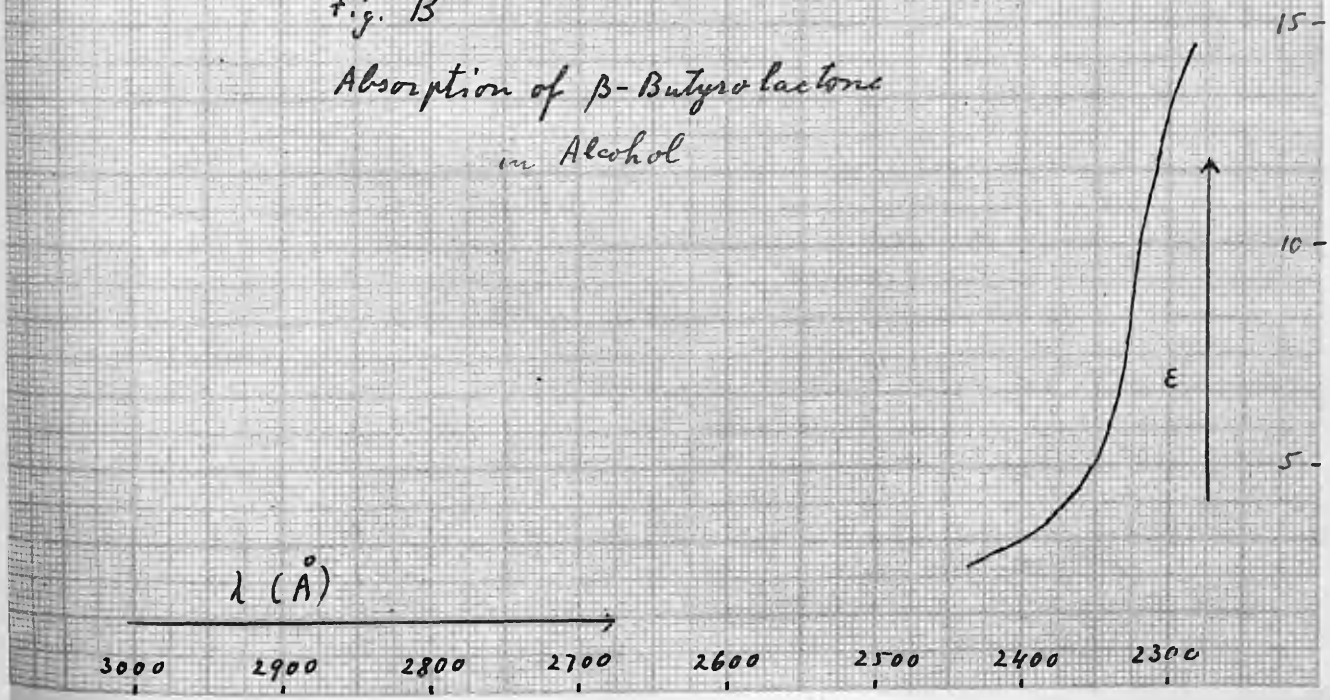


Fig. B

Absorption of β-Butyrolactone

in Alcohol



Absorption of γ-Valerolactone and β-Butyrolactone.

The difference of the shape of the two curves is explained by the fact that for β -butyro lactone and alcoholic solution was used, whereas the readings for γ -valerolactone were taken in hexane. Measurements on β -butyrolactone in hexane (not recorded in the graph) showed that the absorption in this medium is considerably shifted towards the short waves - even beyond the absorption of the valerolactone. The extinction in alcohol may be influenced not only by the polarising effect of this solvent but also by a partial alcoholysis of the somewhat unstable β -lactone.

S U M M A R Y.

As a preliminary to investigating the optical activity of some high rotating compounds of the santonine group, the ultra-violet absorption spectra of parasantonide, santonide, parasantonide-imide, parasantonic acid, santonic acid, santonine and l-desmotroposantonine were studied (Part I, a).

The rotatory dispersion and circular dichroism of the first three compounds were then examined. They show a very strong Cotton-effect connected with an intense absorption band near λ = 3000 Å (Parts Ib and Ic: See also Mitchell & Schwarzwald, J.C.S., 1939, 889). The extreme values for the specific rotations lying between $|[\alpha]|$ = 25,000° and $|[\alpha]|$ = 50,000° and the maxima of circular dichroism lying between $(\varepsilon_l - \varepsilon_r)_{max}$ = 27 and $(\varepsilon_l - \varepsilon_r)_{max}$ = 58, are much higher than the corresponding values of any other substance in homogeneous solution measured up to now. The anisotropy factor $\frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$ is of the usual order of 3.10^{-2}, observed in weak(optically active) absorption bands. The optical activity of the other santonine derivatives could not be investigated in the absorbing regions because of the small anisotropy factors of their bands.

After a brief account of the chemistry of the compounds (Part Id) the absorption spectra of parasantonide, santonide and parasantonide-imide are discussed in the first section of Part Ie. By excluding all alternatives on grounds of chemical evidence and comparative study of the absorption spectra of related substances, the absorption band near λ = 3000 Å is in santonide and parasantonide attributed to a ketonic $\diagdown\!\!\diagup$CO group whose intensity is increased because of vicinal action of other substituents. Examples are cited where a similar increase in the ketonic absorption has been observed. In parasantonide-imide the corresponding band is caused by the ketimino-group. The more intense second band shown by the three substances is due to the absorption of the lactone group. This again is proved by comparing the absorption of the lactones and those of the corresponding hydroxy-acids. Reference is also made to the absorption of simple lactones, which is compatible with the assumption made.

The discussion of the optical activity (Id, second section) includes attempts to apply Lowry and Hudson's modification of Kuhn's formula to parasantonide and santonide. In neither cases can the circular dichroism curve be represented satisfactorily by one term of Gauss's error distribution curve $\varepsilon_l - \varepsilon_r = (\varepsilon_l - \varepsilon_r)_{max} \cdot e^{-\left(\frac{\lambda-\lambda_0}{\sigma}\right)^2}$. The agreement between observed and calculated rotations is not much

better. Better results were obtained for santonide by splitting the observed circular dichroism curve into two components which are indicated by the shape of both absorption and circular dichroism curves, applying the approximation formula to each of them and adding the rotations. The question whether the Cotton-effect in santonide is composite could not be decided because the near coincidence of the wave lengths of maximum absorption, circular dichroism and of the reversal of sign of the rotations does not support the assumption of a composite effect, while the mathematical analysis seems to suggest it. Application of Kuhn's theory leads to a distance between the two coupled oscillators which exceeds the diameter of the molecule. Another contradiction to Kuhn's theory is the fact that an anisotropy-factor of the order of 10^{-2} is exhibited by a strong absorption band of $f \sim 10^{-2}$.

Condon, Altar and Eyring's theory seems more suitable for the qualitative explanation of the effects observed as it postulates the presence of some conditions which in the present case were assumed because of evidence derived from chemical properties and absorption spectra. The extremely high optical activity should therefore be attributed to a very strong asymmetric disturbance exerted

on the motion of the electrons of the ketonic CO-group by a neighbouring substituent - probably the lactone group.

Part II gives an account of the absorption spectrum (measured in water and alcohol), rotatory dispersion and circular dichroism of camphonolactone, a simpler ketolactone where the ketone and lactone group are near to one another. The substance shows an ordinary ketonic absorption band connected with a Cotton-effect. The rotatory dispersion indicates the presence of several contributions of partly opposite sign to the observed rotations. Neither rotations nor circular dichroism are unusually high. The Discussion shows that the conditions supposed to account for the phenomena observed in the santonine derivatives are not present in camphonolactone.

Finally, the absorption of β -butyrolactone and γ-valerolactone is recorded in order to confirm the assumptions made regarding the absorption spectra of the santonine derivatives.

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THE PHOTOLYSIS OF 1-4, DIPHENYL-2-CHLORO-2-NITROSOBUTANE.

The Photodecomposition of 1,4,Diphenyl-2-chloro-2-nitrosobutane.

The photochemistry of chloronitroso compounds has been studied by some authors (1) partly as a problem of considerable interest in itself, partly with a view to find substances which are suitable for asymmetric decomposition, i.e., the partial resolution into its optically active components of a racemate by the action of circularly polarised light. The present investigation on the action of light on diphenyl chloronitrosobutane was carried out with the latter aim in view. Like other aliphatic chloronitroso hydrocarbons, it fulfils the following preliminary conditions: the absorbing group is attached to an asymmetric carbon atom: it is fairly transparent in the spectral region of the absorption band, so that it might be hoped that small rotations caused by the action of light could be detected and - by analogy with the other compounds of this type - it was expected to have a quantum yield of the order of unity. An advantage of diphenyl-chloronitrosobutane compared with other chloronitroso compounds is its readiness to crystallise, and, its stability, which makes its preparation and purification very easy.

A). Preparation of the Substance.

1,4,diphenyl-2-chloro-2-nitrosobutane was first prepared by S. Mitchell according to Piloty's method by passing a stream of dry chlorine through a cooled ethereal solution of 1,4,diphenyl-butanoneoxime (2). Soon after the chlorine starts passing through the solution the latter turns blue and at the same time a voluminous precipitate of the oxime-hydrochloride is formed owing to the liberation of hydrochloric acid in the course of the reaction. The precipitate gradually disappears and soon after it has vanished entirely the reaction is finished. The ether is evaporated and the intensely blue oil that is left crystallises from methyl- or ethyl-alcohol. After 2 - 3 further crystallisations its melting point remains constant at 49°: micro combustion gave the following results:-

	Found	Calculated
C	70.22%	70.24%
H	5.55	5.85
N	5.43	5.12
Cl	13.12	12.96 (Stepanow's method).

The yield is almost theoretical. Cooling is not necessary.

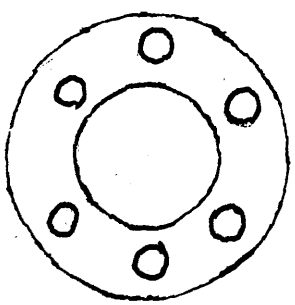
1,4,diphenyl-butanone-oxime was obtained in the usual manner by boiling the ketone with the equivalent amount of $NH_2OH.HCl$ and sodium carbonate with alcohol and

water for half an hour. It can be recrystallised from alcohol or petroleum ether: being a mixture of the two stereo isomers, it has no sharp melting point but rather melts over a range from 106 - 115°. The two forms can be separated by repeated recrystallisations, but this involves great losses and was not necessary for the present purpose(2).

1,4,diphenylbutanone was prepared by oxidation of 1,4-diphenyl butanol with chromic anhydride in acetic acid (2).

B). The Action of Light on 1,4,diphenyl-2-chloro-2-nitrosobutane.

Solutions of the compound were exposed to ordinary electric light in sealed tubes which were almost completely full (to restrict photo-oxidation as far as possible).



The following arrangement provided a sufficiently high intensity of the illumination so as to complete the decomposition of a 5% solution in 12-14 hours. The diagram represents the arrangement seen from above. The inner circle is a large cylindrical glass vessel through which water is circulated and in which the sealed tubes are suspended vertically: the small circles represent 6 60-watt lamps and the large outer circle is a large cylindrical

cover of tin reflecting most of the radiation into the glass vessel.

Decomposition Products.

The decomposition is marked by the disappearance of the blue colour of the chloro-nitroso compound. In methyl alcohol as solvent, the final colour is very faintly greenish - almost colourless. In benzene or carbon-tetrachloride there is a change of colour to yellow. Investigations were confined to the decomposition in methyl alcohol. Hydrochloric acid is formed during the decomposition. Titration with NH_4CNS and $AgNO_3$ showed that the yield of HCl was 99.6% per decomposed moles. In other chloronitroso compounds the amount of HCl - though always over 90% - was smaller, perhaps owing to the greater impurities of these substances which are mostly liquids (3).

When the solvent after completed decomposition is evaporated, a greenish oil mixed with white crystals is left. The solvent was removed under reduced pressure, the temperature always being kept below that of the room. As the oil is much more soluble in methyl alcohol than the crystals, this solvent was used directly for the purification of the crystals. They have no sharp melting point but melt over a range (115-127°). By analogy with the decomposition observed in other chloronitroso compounds, it was first thought that this product might be the oxime

hydrochloride. A sample of the latter substance was consequently prepared by passing a stream of dry HCl through an ethereal solution of the oxime. The voluminous precipitate which readily forms consists of fine crystals melting between 123° and 130° (dec.). Mixed with the crystals of the crystalline decomposition product, a definite lowering in the melting range of the former was observed. When mixed with the diphenyl-butanone oxime, no lowering of the melting range of the latter was observed. Combustion gave the following results:- C 80.55% H 7.19, N 6.22. The theoretical values for the oxime are:- C 80.33, H 7.11, N 5.84. A further identification was necessary particularly in view of the disagreement in the value found for N. The molecular weight was measured by means of Menzies' differential thermometer (M = 236, theor. 239).

The crystalline decomposition product was submitted to steam distillation in the presence of dilute H_2SO_4. An oil was obtained which soon crystallised in the condenser and in the receiver. After two crystallisations from petroleum ether it melted at 46°, which is also the melting point of diphenyl-butanone. Combustion gave C 85.22, H 6.91, the theoretical values for diphenyl-butanone being C 85.7, H 7.14. The mixed melting point with a sample of ketone obtained by vapour distillation of the oxime in the presence of acid was equal to the melting point of the two pure substances. The fact that the

crystalline decomposition product is diphenyl butanone oxime is therefore established beyond doubt.

The decomposition yielded 40 - 50% oxime (% of the theoretical amount of oxime). For the formation of the oxime two atoms of hydrogen are required which are supplied either by a second decomposition product or by the solvent.

If methyl alcohol acts as a donator of hydrogen, formaldehyde should be found among the decomposition products. Search for formaldehyde has been unsuccessful in the photodecomposition of chloro-nitroso-butane (3). To test for CH_2O in the present case the solution contained in the sealed tube was submitted to steam distillation. The first parts of the distillate were diluted with water and added to a solution of dimethyl-dihydroresorcinol (dimedone) in water. A crystalline precipitate was formed after standing for some hours. After recrystallisation from alcohol it melted at 188-189°. The melting point given in literature for the precipitate formed by dimedone and formaldehyde in aqueous solution is 187-188°. The presence of formaldehyde was thus proved. The quantitative determination of the formaldehyde formed during the decomposition was carried out as follows:- after complete photodecomposition the solution was subjected to steam distillation which was stopped as soon as it became

heterogeneous. The condenser was connected to the ice-cooled receiver (which contained water) by means of an adapter. To the distillate 2 g. NH_4Cl and an excess of .5 normal sodium carbonate solution were added. The solution was titrated on the following day with .5 normal H_2SO_4 against methyl orange. Only 1.3% moles CH_2O per moles of decomposed substance had been formed. This fact does not, of course, exclude the possibility that CH_2O is formed in larger quantities since it is possible that most of it disappears again because of polymerisation or other secondary reactions with the reactive radicals or molecules which no doubt are formed in the initial stages of the decomposition reaction.

At any rate other decomposition products had to be found. They were at first looked for in the green oil which is left along with the crystals after the removal of the solvent. As it was found that on addition of ether to the residue the amount of crystalline substance increased, it was hoped to separate the oil from the oxime by its greater solubility in ether. No complete separation could be obtained in this way. Out of the green oil extracted with ether further amounts of oxime crystallised after some days. The bulk of the oil, however, did not crystallise from any of the common organic solvents. Separation could be achieved by precipitating the oxime as hydrochloride out of the ether solution, but the oil did

not crystallise.

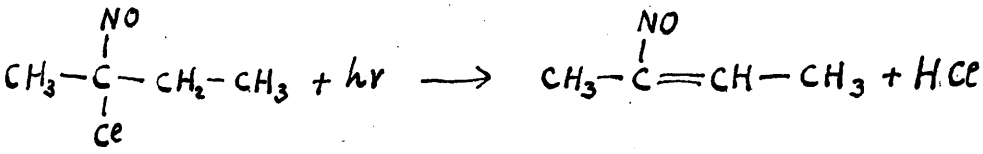
When the green oil was boiled with hydroxylamine-hydrochloride, sodium carbonate and aqueous alcohol crystals were formed: these were identified as diphenyl-butanone oxime. It therefore seems that the oil contains some diphenylbutanone.

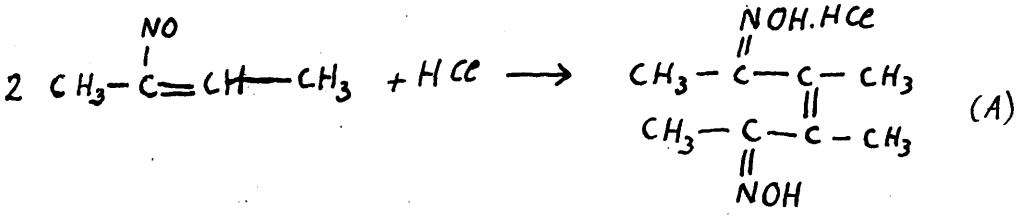
Attempts to isolate a second product in this way having been unsuccessful, the following experiment was carried out:- to the residue after the removal of methyl alcohol, ether and sodium carbonate solution were added. Under these conditions the oxime goes quantitatively into the ether layer (as previous tests showed). From the aqueous layer a white solid is precipitated by dilute acids. Its purification offered considerable difficulties which could not be overcome entirely. It cannot be re-crystallised from the common solvents, being very soluble in some of them (benzene, MeOH, EtOH, ether, esters, dioxan, etc.), insoluble in others (petroleum ether). Crystals were eventually obtained by dissolving the solid in alcohol and adding water gradually. The crystals decomposed at 160° after softening. In the course of some days, however, the decomposition point was considerably lowered although the appearance of the substance remained unaltered. The substance then no longer dissolved completely in benzene or alcohol but left a brownish viscous residue. These complications together with the fact that

this product is obtained with a yield of only 10% of original blue compound and further losses incurred by recrystallisation, make the identification of this product a difficult problem which is beyond the scope of the present physicochemical research.

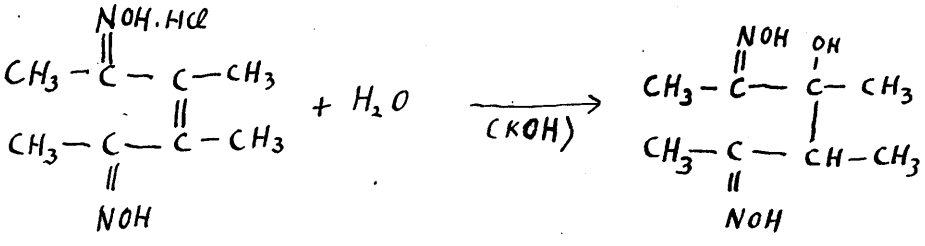
Comparing the decomposition of diphenyl-chloronitrosobutane with that of chloronitrosobutane and other aliphatic chloronitroso-hydrocarbons, the following differences are noted:- 1) there is no evidence for the formation of a double molecule as the main decomposition product in the absence of water(4). A double molecule (A) was formed with a yield of 44% in the case of chloronitrosobutane: only on addition of alkali was the latter split into two products (B) and (C).(5). In the present case the oxime (corresponding to decomposition product (B) in the case of chloronitrosobutane) seems to be formed primarily since it crystallises from the residue after removal of the solvent. The assumption that a double molecule of the type (A) is formed first but dissociates again because of instability, is unlikely for it is hard to see how such double molecule could split up giving rise to the formation of the oxime in absence of water. (Commercial methyl alcohol was dried by repeated treatment with sodium to exclude the possibility of the small amount of water contained in it playing a decisive rôle; but this

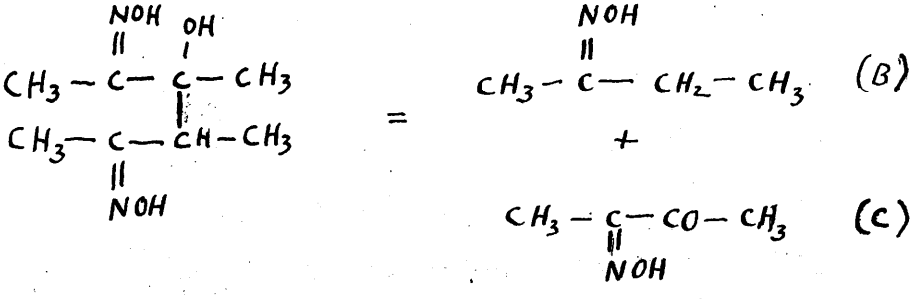
The Photolysis of 2-chloro-2-nitrosobutane according to Mitchell and Cameron (6).





(A)





(B)

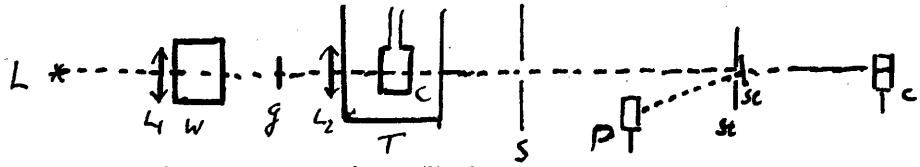
(C)

did not make any notable difference in the decomposition). 2) Formaldehyde is found among the decomposition products although in small amounts. This fact can be interpreted in several ways. a) The formation may be a side reaction involving only 1.3% of the molecules decomposed without influence on the main decomposition reaction. b) The methyl alcohol may play a major part in the process by supplying half of the very unstable molecules formed after the splitting off of HCl owing to the absorption of light (see the mechanism suggested by Cameron) giving rise to the formation of CH_2O which, in turn, may react in some way or other with the other half of the active molecules. This mechanism would explain the fact that the yield of diphenylbutanone oxime does not exceed 50% and the small yield of formaldehyde left after the decomposition; in this case for two molecules of decomposed blue compound, 1 molecule of MeOH is used up. There is finally the possibility that each decomposing molecule reacts with one molecule of MeOH and that part of the diphenylbutanone oxime thus formed quantitatively disappears because of a secondary dark reaction with CH_2O. The possibility that the formaldehyde causes a dark decomposition of the blue compound may be discarded since in this case the quantum yield should be definitely higher than in the case of compounds whose decomposition does not give rise to the formation of CH_2O. The reverse is true.

The experimental evidence gained does not allow any choice between the possibilities mentioned above. There is merely an indication that at least part of the hydrogen required to form the oxime comes from decomposition products rather than from the solvent. Analysis of the second crystalline decomposition product described above shows that it contains less hydrogen than the oxime or than any compound which may be formed by condensation with or addition of CH_2O in which case the value for H found by analysis would be higher.

Measurement of the Quantum Yield.

The quantum yield of diphenyl-chloronitrosobutane was measured by the method developed by Mitchell and Cameron with the modifications introduced by Mitchell and Simpson (6). As the method has been described in full detail elsewhere (7), only a brief outline will be given here. The diagram below shows the optical arrangement. The light source (L) is an automatic carbon arc. It is run



from the D.C. mains with 7.5 amps. L_1 is a lens and W a water filter (absorbing most of the infra-red radiation). g is an ordinary red glass filter. The thermostat T is

so placed that the lens L_1 focuses the image of the arc on its front wall. The lens L_2, immediately in front of the wall of the thermostat, focuses the light on the surface of the cell containing the solution of the substance under investigation. Inside the thermostat there is the Christiansen filter (a trough containing a mixture of powdered Crown glass and methyl benzoate) which transmits only a narrow spectral region of light which varies with the temperature of the thermostat. S is an ordinary shutter by means of which the illumination is controlled. St is a circular stop cutting out most of the impure light. sl is a thin glass slab through which most of the light passes to the surface of the cell c, where it is completely absorbed. A small fraction is reflected to the surface of the Weston-photronic cell P.

Method.

The quantum yield is the ratio of the number of molecules decomposed to the number of light-quanta $h\nu$ absorbed. It is therefore necessary to measure, (a) the amount decomposed, and (b) the energy absorbed by the solution. (a). The amount of decomposition is measured colorimetrically. For this purpose a Weston photronic cell is placed close behind the cell c. The photocell is connected with a sensitive mirror galvanometer. The carbon

arc is replaced by a 12 volt filament lamp run from accumulators, and the deflection of the galvanometer is measured. Readings are taken for a number of solutions of known strength. From a graph where the log of the deflection is plotted against the concentration the unknown concentration can be determined. Owing to the absorption of the blue compound the unknown solution must be diluted three times for the measurement.

(b) The amount of energy absorbed equals the amount of energy radiated into the cell, the absorption being complete. The amount of energy radiated into the cell equals average intensityx(time of illumination). The average intensity of the light is recorded with the help of the photocell P which is connected with a mirror galvanometer whose deflection is recorded photographically on a rotating drum. As the deflection is proportional to the intensity of the light radiated into the cell, the factor by which the deflection is to be multiplied in order to obtain the intensity of the light must be found. This is done by replacing the cell c by a calibrated thermopile connected with a mirror galvanometer. By a series of illuminations with light of the wave-length required for the decomposition, the ratio of the deflection of the galvanometer connected with the thermopile to that of the galvanometer of the photocell is found (a_2). The intensity of the illumination during the decomposition = deflection of the galvanometer.

connected with the photocell x ratio $\frac{\text{thermopile defl.}}{\text{photocell defl.}}$ x calibration factor of the thermopile.

Preliminary Measurements and Adjustments.

The temperature of the thermostat is so chosen that the Christiansen filter transmits the wave length for which the absorption of the solution has its maximum. Cameron (8) has recorded the calibration graph for the filter giving the wave length of maximum transmission as a function of the temperature. The correctness of the graph has been checked for the required wave length of 6580 Å by means of a spectroscope.

The thermopile was calibrated with a standard Hefner candle burning at 1 m. distance from the surface of the thermopile. The arrangement has been described by Cameron (9). By a series of illuminations and dark periods of equal duration the average deflection is found. It corresponds to the intensity of 2.25 x 10^{-5} x surface area of the thermopile (Gerlach

Calculation of the quantum yield: $\frac{\text{gm.mol. decomp.}}{\text{energy abs. cal.}} \times \frac{28470.}{\lambda\,(m\mu)}$ The energy absorbed during the experiment is equal to time (in sec.) x a_1 x a_2 x 1.05 (aver. deflection on the recording drum) cal. The factor 1.05 is a correction for the loss of light through reflection on the glass which protects the thermopile against heat radiation. The equation, of course, holds only if the exposed surface area of the thermopile is equal to the

illuminated surface of the cell c containing the solution.

As the wave length of maximum absorption as well as the extinction coefficient for that wave length are required in order to obtain a solution which absorbs the light completely (not more than 1% of the irradiated light should be transmitted), the extinction curve of the substance must be measured.

Absorption Spectrum (Table I Fig.1)

The absorption curve of 1,4 diphenyl-2-chloro-2-nitrosobutane was recorded by means of a Spekker spectrophotometer (A.Hilger). Table 1 gives the readings and Fig.1 shows the curve. The maximum of the absorption band lies at λ = 6580 Å and it amounts to ε = 24.8. The shape of the curve on the short wave length side indicates the presence of a subsidiary band similar to that observed by Mitchell and Simpson (10) and Simpson (11) in some chloronitroso compounds. The maximum extinction is a little higher than that in the case of most other chloronitroso compounds investigated and it lies at longer wave lengths because of the size of the molecule and the influence of the phenyl groups (12).

Results of the Measurement of the Quantum Yield.

The temperature of the thermostat containing the Christiansen filter was kept at 15.2° corresponding to a maximum transmission for λ = 6580 Å. A 6.5% solution of the compound

in dry methyl alcohol was used. The solvent was freed from the bulk of oxygen dissolved in it by passing nitrogen through it. The decomposition was allowed to reach 10% because the error caused by transmission of a solution weaker than 5.8% in a 1 cm. cell is appreciable. Higher initial concentrations could not be used because of the small solubility of the substance in methyl alcohol.

The results of two typical experiments are given in Tables 2 and 3. In one case the quantum yield = 0.89: in the other 0.82.

Discussion.

The result obtained is somewhat surprising: all chloronitroso compounds (including chloronitroso hydrocarbons (12) and chloronitroso acids and -acid-esters (13)) had a quantum yield greater than 1. It was therefore at first thought that the result obtained in the present case was due to some fault in the experimental arrangement. The latter was checked by measuring the quantum yield for the decomposition of methyl-chloronitrosobutyrate by light of λ = 6350 Å in acetone. The result obtained was φ = 1.23 in good agreement with the value of φ = 1.19 found by Simpson (14). Moreover, for diphenyl chloronitrosobutane $\varphi < 1$ in all the measurements.

It would therefore appear that there is a difference in the decomposition reactions of the diphenyl-chloronitrosobutane on the one hand and that of the other chloro-

Absorption Spectrum of 1,4 Diphenyl-2 -chloro-2 -nitrosobutane.

0·5093g in 25 cm³ alcohol

λ (Å)	$\log I/I_0$	ε	λ (Å)	$\log I/I_0$	ε
7450	0.1	1.33	6450	1.6	21.52
7115	0.3	4.03	6415	1.5	20.14
6960	0.6	8.01	6380	1.4	18.79
6875	0.7	9.40	6355	1.3	17.48
6840	0.8	10.74	6333	1.2	16.12
6820	0.9	12.09	6300	1.1	14.77
6800	1.0	13.43	6250	1.0	13.43
6775	1.1	14.77	6100	0.9	12.09
6760	1.2	16.12	6005	0.8	10.74
6750	1.3	17.48	5950	0.7	9.40
6740	1.4	18.79	5900	0.6	8.01
6720	1.5	20.14	5840	0.5	6.71
6700	1.6	21.52	5690	0.4	5.37
6650	1.7	22.85	5580	0.3	4.03
6500	1.7	22.85			

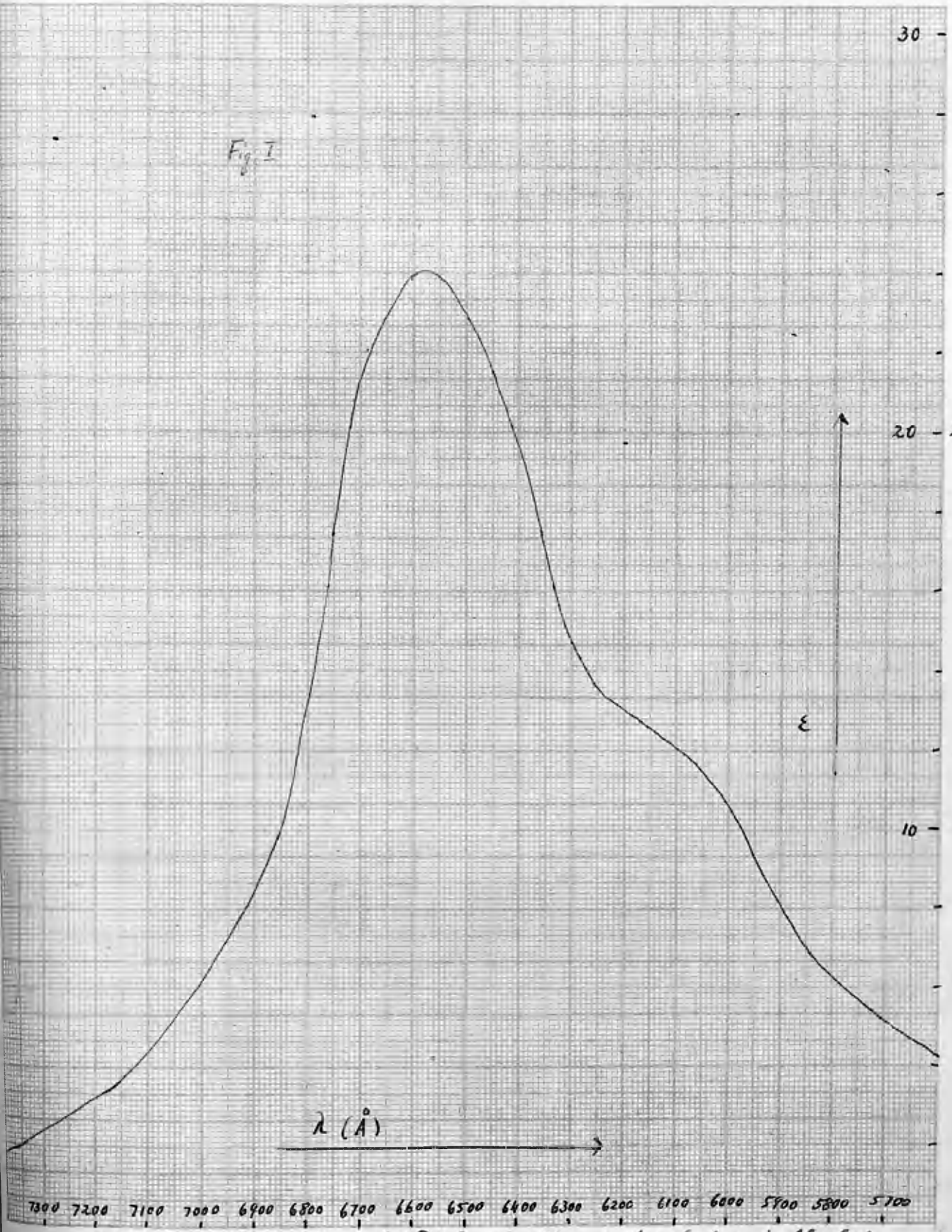


Fig I Absorption Spectrum of 1,4 Diphenyl-2-chloro-2-nitrosobutane in Alcohol

Table(2). Quantum Yield for the Decomposition of 1,4 Diphenyl 2 chloro 2 nitroso butane by light of λ = 6580 Å.

Dry Methyl Alcohol freed from Oxygen

Volume of the cell = 4.00 cm^3. M = 273.5

Initial Concentration .. 6.525%

Final Concentration .. 5.926%

Gm. mol. decomp. $= 4 \times \frac{6.252 - 5.926}{273.5 \times 100} = 0.876 \times 10^{-4}$

Recorded average deflection = 12.3 cm.

Average ratio a_2 = 3.8

Illuminated area = 2.546 cm^2.

Deflection with Hefner Candle = 6.66 cm.

Calibration factor $(a_1) = \frac{2.546 \times 2.25 \times 10^{-5}}{6.66} = 8.60 \times 10^{-5}$ cal/sec.

Time of illumination = 10,500 sec.

Energy Absorbed = $1.05 \times 8.60 \times 10^{-5} \times 12.3 \times 10{,}500 \times 3.8$

= 4.43 cal.

$$\mu = \frac{0.876 \times 10^{-4}}{4.43} \times \frac{28{,}470}{658} = 0.876.$$

Table (23). Quantum Yield for the Decomposition of 1,4 Diphenyl-2-chloro-2-nitrosobutane by light of λ = 6580 Å.

Dry Methyl Alcohol freed from Oxygen

Volume of the cell = 4.00 cm^3. M = 273.5.

Initial Concentration = 6.524 gm/100 cm^3.

Final Concentration = 5.904 gm/100 cm^3.

Gm. mol. decomp. = $\frac{4 \times 0.620}{100 \times 273.5} = 0.834 \times 10^{-4}$

Recorded average deflection = 12.9 cm.

Average ratio a_2 = 3.42 cm.

Illuminated area = 2.546 cm^2.

Deflection with Hefner Candle = 6.66 cm.

Calibration factor (a_1) = 8.60×10^{-5} cal/sec.

Time of illumination = 11,040 sec.

Energy Absrobed = $1.05 \times 8.60 \times 10^{-5} \times 12.9 \times 3.42 \times 11{,}040$

= 4.40 cal.

$$\mu = \frac{0.834 \times 10^{-4}}{4.40} \times \frac{28{,}470}{658} = 0.819.$$

nitroso compounds on the other. The fact that $\varphi < 1$ must be explained by partial deactivation of the molecules which have absorbed a quantum of light before they decompose. Deactivation can occur in three ways: a) by intramolecular deactivation, i.e., the dissipation of the absorbed energy to other parts of the molecule, b) by collision, and c) by the influence of a dark reaction on the quantum yield.

a). The dissipation of energy is more likely in a large molecule than in a small one since, according to the equi-partition of energy, the concentration of it in one part of the molecule is much more unstable thermodynamically - and therefore has a shorter lifetime - in large molecules than in small ones. There may, moreover, in the present case, be a more direct influence on the electronic structure of the N=O group, which makes possible the electronic transitions leading to the transfer of energy which are "forbidden" in the case of simpler molecules.

b). Deactivation by collision is less likely in the present case than in the case of simpler compounds because the steric factor of the collision with the activated part of the molecule must be smaller in diphenyl chloronitrosobutane because of the shielding effect of the large phenyl groups against approaching molecules.

c). There is, however, another possibility by which the shielding influence of the phenyl radicals may cause a lowering of the quantum yield. This would happen if the

reaction leading to decomposition is bimolecular, i.e., if the activated molecule decomposes only after collision with another molecule. Such a mechanism is compatible with a quantum yield of $\varphi \sim 1$ if the bimolecular reaction is fast compared with the primary process of absorption. In this case the rate of decomposition is determined by the rate of the primary process and independent of the concentration of the solution. (Cameron (15) found that the concentration does not influence the quantum yield). If the steric factor for the bimolecular reaction for the diphenyl compound is small compared with that of other chloronitroso compounds, it is possible that for the former the rate of the bimolecular dark reaction is no longer large compared with the rate of the primary process so that the average time which elapses before the activated molecule is decomposed by collision is greater; hence the chances for deactivation are increased.

Unfortunately the experimental evidence does not decide between the possibilities a) and c). If the mechanism is influenced by the bimolecular dark reaction, variation of the quantum yield with the concentration should be observed. This could not be done since the concentration could not be varied owing to the small solubility of the compound in MeOH on the one side and the necessity for total absorption on the other. Using thicker layers would

overcome the latter difficulty, but that necessitates other inconveniences such as a longer time of exposure, etc. It is not unlikely that both a) and c) play a part in the mechanism of the reaction.

As the yield of the HCl formed during the decomposition in all chloronitroso compounds is between 90-100% independently of the other decomposition products, the splitting off of HCl was assumed to be the process following absorption. Cameron has suggested that the energy of the light quantum was passed on to the neighbouring C-atom where a hydrogen nucleus was split off, but this assumption is not in agreement with the energy involved. The absorbed light provides an energy of 40-45 $Cal/_{Mol}$, the rupture of a C-H bond requires 97 ± 5 $Cal/_{Mol}$ (17). The energy necessary to split off HCl does not, however, exceed the absorbed energy. Brearley, Kistiakowsky & Stauffer (18) found that the energy of activation for the reaction tertiary butyl chloride $\longrightarrow$ HCl + isobutylene = 45,000 $\pm$ 1900 $cal/_{mol}$, and that for the analogous reaction of tertiary amyl chloride 46,000 $\pm$ 700 cal. It may therefore be assumed that the splitting off of HCl does not consist in the separate rupture of the C-H and of the C-Cl bonds (for which $\sim$ 170 cal would be required) but that before decomposition some kind of link is formed between the H and the Cl with simultaneous weakening of the C-H and the C-Cl bonds. While the Cl atom in chloronitroso compounds

is not attached to tertiary carbon atoms, it is probably bound more loosely owing to the presence of the negative substituent N=O at the same carbon atom. (The large dipole moment of the $-\overset{+}{N}=\overset{-}{O}$ 1.9×10^{-18} (19) will reduce the moment of the C-Cl bond by inducing a dipole moment of opposite sign $\overset{\pm}{Cl}-\overset{-}{\overset{+}{C}}-\overset{+}{N}=\overset{-}{O}$ and thus weaken the C-Cl bond.) The activation energy for the formation of HCl which is largely determined by the stability of the C-Cl and the C-H links should be equal to or smaller than that observed for the decomposition of the tertiary alkyl chlorides. In this case the energy of the light (of λ = 6580) $\cong$ 42,800 $Cal/_{Mol}$ together with the thermal energy at room temperature is sufficient to split off HCl. It seems that this process has the quantum yield of the order of 1, whereas the secondary reactions of the radical

$R_1 - \overset{NO\cdots}{\overset{|}{C}} \cdots C - R_2$ which is left, depend on the nature of R_1 and R_2. In some cases these radicals dimerise (6): in others (including the present one) they dehydrogenate other molecules with formation of oxime.

S U M M A R Y.

The preparation is described of 1,4 diphenyl-chloronitrosobutane. The decomposition products are investigated, HCl (99.6%), diphenylbutanone oxime (50%) and CH_2O (a small amount) are found. The absorption spectrum is recorded and the quantum yield measured for the decomposition by light of the wave length of maximum absorption. $\bar{\gamma} = 0.85$, which is less than the values previously found for other chloronitroso compounds (which were slightly > 1 in all cases). The result is discussed and it is shown that the energy of the absorbed light is sufficient to split off hydrochloric acid. The secondary dark reactions of the primary decomposition products do not influence the quantum yield.

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